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Health Effects Research Lab, Research Triangle Park, N C

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Ecological Research Series



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THIRD ANNUAL CATALYST RESEARCH PROGRAM REPORT

by

Health Effects Research Laboratory
Research Triangle Park, N.C. 27711

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
HEALTH EFFECTS RESEARCH LABORATORY
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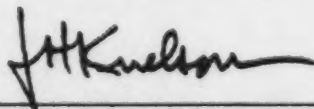
This report has been reviewed by the Health Effects Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The Health Effects Research Laboratory, Research Triangle Park, conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides as well as other chemical pollutants. The Laboratory develops and revises air quality criteria documents on pollutants for which national ambient air quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is preparing the health basis for non-ionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of health care and surveillance of persons having suffered imminent and substantial endangerment of their health.

New technologies for controlling emissions of pollutants to the atmosphere are always a welcome advance in the pursuit of a cleaner environment through research. A thorough study of these new technologies is in order, however, to assure that the net effect on public health is beneficial. The Catalyst Research Program, in its investigation of the automotive oxidation catalyst, provides a sound base upon which the EPA can make a responsible assessment of the effect on public health of this advanced emission control technology.



John H. Knelson, M.D.
Director
Health Effects Research Laboratory

PREFACE

The Catalyst Research Program, initiated in FY 1975, is a broad multidisciplinary research effort to provide a sound technical basis for evaluating the public health issues related both to the benefits associated with the reduction of regulated emissions and to the potential health hazards associated with any unregulated emissions generated by control systems. This report covers work performed during the third year of the Catalyst Research Program plus related work performed outside the CRP.

ABSTRACT

This report constitutes the third annual report by the Office of Research and Development on the Catalyst Research Program (CRP) required by the Administrator as noted in his testimony before the Senate Public Works Committee on November 6, 1973. It includes all research aspects of the broad multidisciplinary program including: emissions characterization, measurement method development, monitoring, fuel analysis, toxicology, biology, epidemiology, human studies, and unregulated emissions. Principal focus is on catalyst-generated sulfates and other nonregulated emissions, including particulate emissions from light-duty diesels.

Highlights in this report are:

- Results of continued tests of sulfuric acid emissions from catalyst-equipped vehicles are such that these emissions may be considered much less of an air quality problem than was previously hypothesized.
- With freeway density of catalyst-equipped cars rising to 30 percent in 1976, roadside sulfate readings rose only 10 percent while a 25 percent decrease was observed in carbon monoxide, lead, and total suspended particulates.
- Tests conducted to date show very high particulate emissions from light-duty diesel vehicles, about 25 times the values obtained from catalyst-equipped gasoline vehicles.

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I. INTRODUCTION

Section 202 of the Clean Air Act of 1970, as amended, required substantial reduction in certain specified emission products from automobiles. The automotive industry, to achieve these reductions, chose the oxidation catalytic converter as a primary method of emission control for model year 1975. Subsequent to this decision, EPA intensified its research program to determine what, if any, new pollutants might be emitted into the atmosphere as a result of the application of this technology. The effects of fuel composition and fuel additives on these, as well as regulated, emissions were also studied. Results from the EPA research program indicated that though emissions of hydrocarbons, carbon monoxide, and certain organics would be dramatically lowered, sulfuric acid aerosol emissions would increase, and slight emissions of platinum, palladium, and alumina might also be expected.

Because existing ambient concentrations of sulfates in many areas of the country have been shown to be at levels sufficient to cause concern, and because very little information existed regarding health effects of platinum or palladium as air pollutants, EPA initiated a broad research program to examine the public health impact of catalyst-emitted sulfates, platinum, and palladium.

In testimony to the Public Works Committee of the U.S. Senate, Administrator Train specified EPA's planned program of catalyst-related research:

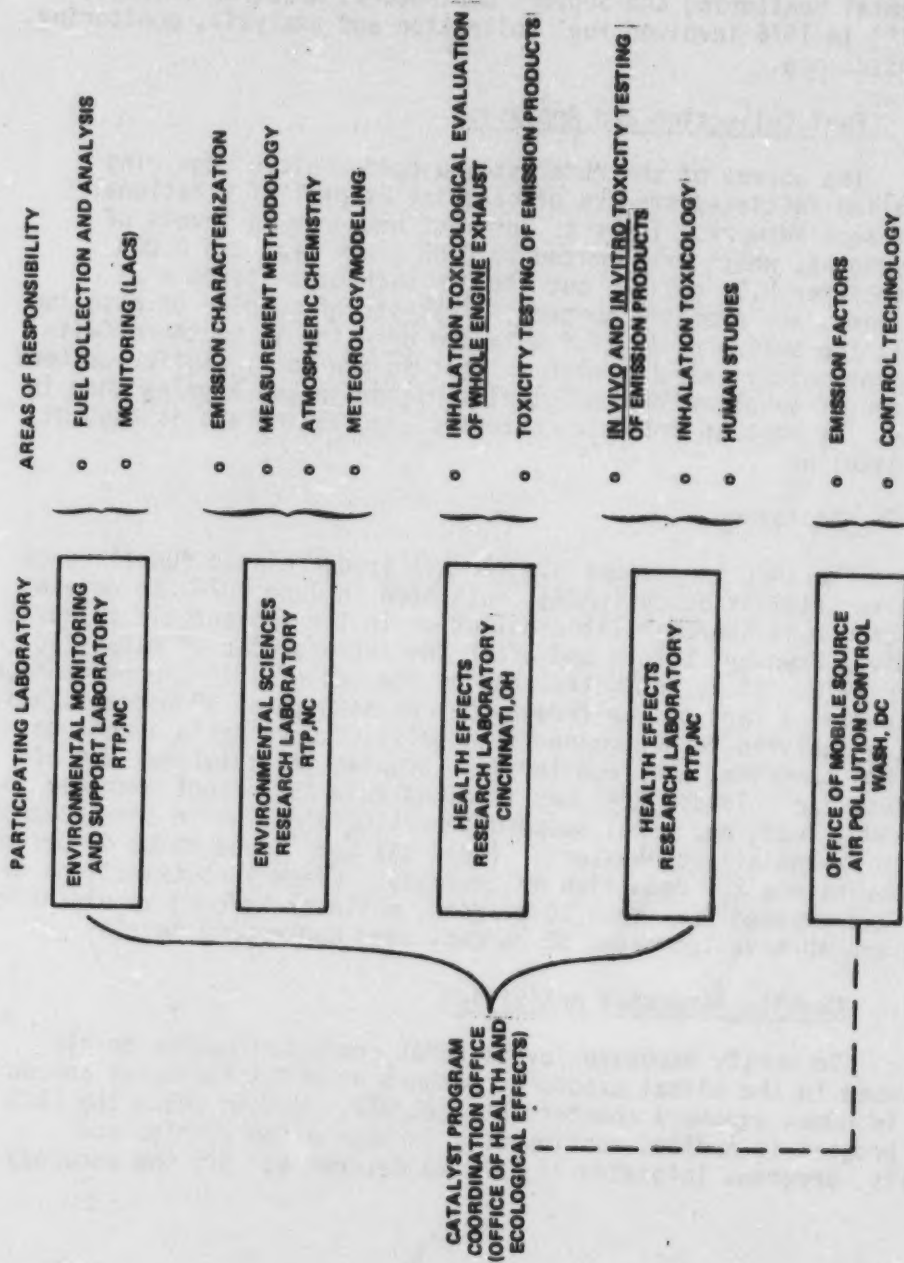
- Accelerate work on development of a reliable test procedure for automotive sulfate emission measurement.
- Consider all feasible alternatives for automotive sulfate emission control.
- Improve the Agency's ability to estimate the public health impact of sulfate and other automotive emissions.
- Improve understanding of the atmospheric chemistry involved in these emissions and initiate an appropriate air monitoring program.

From these broad objectives defined in Administrator Train's testimony of November 1973, an extensive interdisciplinary research program was developed utilizing the resources of EPA's technical staff in the Office of Research and Development and the Office of Air and Waste Management as well as extramural (contracts and grants) programs with the scientific community. The program is now in its third year. The results of the first two years' work were summarized in the first and second annual reports published as EPA reports (EPA-600/3-75-010a through j, dated September 1976, and EPA-600/3-77-008, dated January 1977). This report is the third in a series planned for annual issuance through at least 1978.

The third report, like the second, presents the contents arranged according to the laboratory organization under whose management the projects were performed. This organization is intended to facilitate reporting requirements and to aid in the identification of responsible program management in order to fulfill the requests of report users for further information.

This year, for the first time the individual program reports which were published as separate supplements in the first and second editions, are included as section IV of this document. These reports present the work performed as part of the Catalyst research Program by each of the following groups: Health Effects Research Laboratory, Research Triangle Park, N.C.; Environmental Monitoring and Support Laboratory, Research Triangle Park, N.C.; Environmental Sciences Research Laboratory, Research Triangle Park, N.C.; Health Effects Research Laboratory, Cincinnati, Ohio; and Office of Mobile Source Air Pollution Control, Washington, D.C. An overview of the organization's work is included in each report. In addition, the figure entitled "Organization of the Catalyst Research Program" presents a graphic overview of the research responsibilities of the five organizations participating in the Catalyst Program.

Immediately following the overviews in the summary report, "Program Highlights" focuses on particular areas of research and is organized according to the various pollutants studied rather than according to laboratory. This section provides a brief discussion of the highlights of CRP research in 1976 on sulfates, hydrogen cyanide, manganese, polynuclear aromatic compounds (PNA), ammonia, ruthenium, platinum, and on diesel and whole catalyst emissions.



Organization of the Catalyst Research Program

II. OVERVIEW OF COMPONENT PROGRAMS

A. Environmental Monitoring and Support Laboratory/Research Triangle Park

The work related to the Catalyst Research Program performed by the Environmental Monitoring and Support Laboratory, Research Triangle Park (EMSL/RTP) in 1976 involved fuel collection and analysis, monitoring, and quality assurance.

1. Fuel Collection and Analysis

The advent of the catalyst-equipped vehicle requiring unleaded gasoline initiated studies of gasoline as part of a National Fuels Surveillance Network. There is interest not only in levels of lead and phosphorus, which are limited to 0.05 grams lead and 0.005 grams phosphorus per U.S. gallon, but also in such other factors as sulfur, manganese, and aromatic content. Analysis of samples of gasoline indicated that the sulfur content of unleaded gasoline in Southern California is approximately twice as high as that in New York. Sulfur content in all 3 grades of gasoline is consistently higher in Los Angeles than in San Francisco. Percent of aromatic content is increasing and is highest in unleaded gasoline.

2. Monitoring

The EMSL is responsible for all study-related functions of the Los Angeles Catalyst Study (LACS), initiated in June 1974, to develop information on mobile source-related pollution in the ambient air adjacent to the San Diego Freeway, before and after the introduction of catalytic converters in 1975. It is estimated that by the end of 1976 the percentage of catalyst-equipped cars on the freeway may be as high as 30 percent, and data are being analyzed to determine the catalytic converter's impact on sulfate, carbon monoxide, and lead levels. Studies indicate that the use of the catalyst and unleaded fuel has resulted in a 25 percent decrease in carbon monoxide, lead, and total suspended particulates, while the background levels remain essentially consistent. (Lead has been found to be 60 percent on weekends despite a 20% reduction in traffic). Freeway contributions of sulfates have increased less than 10 percent, while background levels decreased. Oxides of nitrogen have increased 50 percent over background levels.

3. Quality Assurance Activities

To verify exposure levels, EMSL conducted audits on air pollutants used in the animal exposure chambers at HERL/Cincinnati and on those used in human exposure chambers at HERL/RTP. Within EMSL, the LACS monitoring program is audited continuously through blind samples and sample splits, programs initiated in 1974 to determine: (1) the accuracy

achieved by the Rockwell Air Monitoring Center (RAMC); (2) the comparability between analysis performed by RAMC and EMSL; and (3) analytical variability on real air samples. Both programs have changed to accommodate fluctuations in the number of samples collected, variability of the analytical results, and EMSL's growing experience in conducting external audits. Through this quality assurance program, an extensive body of ambient roadside air quality data of known quality has been collected.

B. Environmental Sciences Research Laboratory/Research Triangle Park

The research efforts of the Environmental Sciences Research Laboratory during the 1976 calendar year have been mainly focused on 4 areas: measurement methods, emissions characterization, in-roadway studies, and modeling.

1. Measurement Methods

Several developments grew out of the studies in measurement methodology. A sulfuric acid sampler/analyzer was developed, tested, and modified. A sulfuric acid generator to deliver particles in the 0.02 - 0.5 μm size range was developed and was coupled to an animal exposure chamber at HERL. Projects were initiated to develop a flame photometric detector for continuous in situ measurement of total particulate sulfur and certain individual sulfur compounds and to develop methodology to selectively measure sulfuric acid in the range of 0.25 to 50 $\mu\text{m}/\text{m}^3$. The latter project has identified 3 reagents which can be selectively analyzed in the presence of sulfate, demonstrated the formation of adducts, and has determined their likely composition. Yet another study, a gas chromatographic system, has been created which will permit the analysis of part-per-billion concentrations of NH_3 . A portable dichotomous aerosol collection system to collect atmospheric sulfuric acid in particles smaller than 3.5 μm was developed, and an evaluation was conducted of potential interferences. Results have indicated the strongest potential interference is from gaseous ammonia. However, it was shown that by using an ammonia denuder this is no longer a problem. In addition, if the sampling period is kept to 1 hour or less, sulfuric acid interaction with other particles on the filter is minimal. Prototype instrumentation for SO_2 , NH_3 , NO_x , and H_2S was evaluated using a mobile van equipped with a mapping and data acquisition system.

2. Emissions Characterization

The year's work on emissions concentrates on two issues which have not yet been studied adequately. The first involves a study of sulfuric acid emission factors for 101 in-use California cars. The study revealed that sulfuric acid emission decreases rapidly with increasing mileage, indicating that catalysts lose their sulfate-forming activity more readily than their capacity for hydrocarbons and carbon monoxide. The study has shown that HC and CO remain low for the first year in California cars, that NO_x emissions rates for '75 and '76 model years are mostly greater than California standards,

and that California fuel sulfur levels are about the same as the national average. These samples were collected from the test car tanks; data obtained from samples collected at individual service stations (see page 17) indicate that sulfur levels are higher than the national average. Reasons for this apparent discrepancy are unclear at this time.

The second sought to determine H_2S , COS , NH_3 , HCN , N_2O , H_2SO_4 , and particulate emissions from vehicles with rhodium-containing catalysts under standard and malfunction conditions. Results indicate that catalyst-equipped cars operating under normal conditions yield little HCN and that rich malfunctions increase HCN and CO emissions.

3. In-Roadway Study

An in-roadway study involving scientists from the University of Minnesota, Washington University of St. Louis, and the California Institute of Technology, with support from Rockwell International, was conducted in October 1976, to determine sulfate levels in the roadway and to determine the feasibility of making in-roadway measurements with instruments installed in moving vehicles. The measurements showed that: (a) the sulfuric acid emitted by catalyst-equipped cars is in the nuclei mode ($0.1 \mu m$) particle size range; (b) the emitted sulfuric acid is dispersed and may be neutralized in such a way that the population primarily at risk is the vehicle occupants in the roadways; (c) the highest freeway concentrations of sulfates due to vehicle emissions observed in the two-week experiment during October of 1976 were below $2 \mu g/m^3$; and (d) the ammonia concentrations appeared to be great enough to neutralize the sulfuric acid emitted from the vehicles.

During the spring of 1978, an in-roadway sampling program with measurements both on the roadway and at background sites will be conducted for approximately 30 days using improved H_2SO_4 sampling and analytical methods currently under development. The experimental sampling program will be statistically designed, based on models prepared during 1977 so as to ascertain the exposure risks that can be anticipated in the future. Since the test vehicles will also be monitoring in-roadway NO_2 , the statistical analysis of the measurements may also provide an estimate of the NO_2 exposure to vehicle occupants.

At the inclusion of the in-roadway Los Angeles study, an experiment will be conducted in Research Triangle Park, North Carolina, to measure the H_2SO_4 inside vehicles driving immediately behind a cluster of several high-sulfate emitting automobiles.

4. Modeling

Due to the complexity and great number of variables such as atmospheric turbulence, wind changes, pressure/temperature differentials, and turbulence from vehicle motion, the progress in developing acceptable models of in-roadway conditions has been tedious. To explain how H_2SO_4 mist

reaches the exposed public from catalyst-equipped vehicles, the basic theory of dispersion and aerosol coagulation has been examined in models. A Gaussian model of a line-source roadway has been used with data from General Motors proving-ground-track experiments. Both short-time-scale (second to second) and half-hour meteorological data were applied to the model. Results indicate that assigning Gaussian dispersion parameters on the basis of atmospheric stability alone leads to overestimation of half-hour sulfuric acid concentrations. To improve the predictive capability of this simple theory, best-fit Gaussian distribution parameters were extracted from the GM short-time-scale meteorological data. Analysis of these data will continue into early FY-78. The predictive error found in this approach may be due to the inability to account for the short-term wind meander under low wind conditions or to non-Gaussian concentration profiles induced by cars.

Models incorporating greater physical detail to improve predictive capability are being tested. Numerical integration of the conservation of mass equations may produce a better picture of the roadway as a line source. Techniques using computer programs to perform calculations have been developed and tests are projected for future work. Although GM data are valuable and useful, they have been shown to be limited. More extensive data are being obtained in an ESRL-supported study on the Long Island expressway. These data may allow more extensive evaluation on various models and identify problem areas in prediction.

Changes in automobile and fuel technology are occurring rapidly in response to pollution control and energy conservation challenges. These induce new requirements for quick assessment of environmental impact which engender the development of new models to apply to new problems.

More detailed discussions of each project together with tabular data is available in the Environmental Sciences Research Laboratory report (Appendix B).

C. Health Effects Research Laboratory (HERL)/Cincinnati

The Catalyst Research Program (CRP) at the HERL/Cincinnati location began studies in 1973 to provide data on the toxicology of whole automotive emissions with and without the catalytic converter, and on certain individual pollutants which comprise whole exhaust. A new facility for collecting data on animals exposed to automotive emissions was constructed and fitted with new equipment to replace the previously used Laidlaw Avenue installation. The new facility is able to generate either gasoline or diesel exhaust atmospheres for a broader range of tests. It allows the assessment of effects on inhalation of irradiated (artificial sunlight) and non-irradiated exhaust on biological parameters related to general health and immunity. The relocation, installation, and calibration on the new facilities at the EPA Center Hill Road laboratory delayed the initiation of certain segments of the 1976 research program in Cincinnati.

The CRP effort has been divided into two major segments:

- Assessing biological effects of total exhaust which has been processed by an oxidative catalytic converter.
- Toxicology of single pollutants associated with the oxidation catalyst.

The HERL in Cincinnati works to gather information to determine the biomedical consequences of exposure to automotive emissions which may lead to an improved understanding of those consequences.

The National Research Council document on Fuels and Fuel Additives for Highway Vehicles and Their Combustion Products points out that hundreds of compounds are present in vehicle exhausts which are practically impossible to detect and measure for toxicology studies. Rather than try to create individual components synthetically and then mix them for research, it may be more realistic to use whole emissions from actual working models to achieve more representative results. Biological hazards from interaction of the components--synergism or potentiation--can be just as important as the toxic effects of single isolated components. The CRP provides data on the toxic effects of animal exposure to whole emissions of engines with or without catalytic converters.

A secondary aspect of the program is to study metabolic and biological effects of platinum, palladium, and other nonregulated pollutants (such as H_2SO_4) associated with the use of catalytic converters.

Since the use of catalytic converters in auto exhausts, aerometric data show a decrease in carbon monoxide and hydrocarbon concentration. As sulfuric acid, a product of the catalysts, is a greater irritant than sulfur dioxide (SO_2), its effects could offset the benefits provided by catalytic converters. An additional study, therefore, was initiated in 1976 in which an engine-catalyst combination producing high levels of sulfuric acid would be used with gasoline containing increased levels of sulfur. This was to assess the effects on the respiratory system. The study was also designed to examine animal adaptation to the test atmosphere. The results of this study will be available in 1977.

The CRP at HERL/Cincinnati has four major areas of research all involving assessment of biological effects in laboratory animals exposed to automobile emissions: (1) automotive catalytic emissions, (2) diesel emissions, (3) ultrafine sulfuric acid and metal sulfates, and (4) manganese compounds associated with the use of the additive methylcyclopentadienyl manganese tricarbonyl (MMT) in gasoline.

1. Physical Facilities

Automobile engines used were selected on the basis of wide distribution in the real environment, and thereby functioned as representative sources of emission. Two 1975 automobile gasoline engines and one automobile diesel engine are used in the models for this research. The gasoline engines are equipped with pelletized noble-metal oxidation catalytic converters. To simulate reality more closely, the emissions are channeled into mixing chambers and irradiation (artificial sunlight) chambers before reaching the animal exposure areas which are monitored continuously for gases and particulates of interest to the study by various appropriate methods. Typical gasoline and diesel fuels were selected as representative samples.

2. Automotive Catalytic Emissions Study

Using a 1975 Chevrolet engine with a catalyst, experiments were begun in 1976 to study effects of exposure on pulmonary function in guinea pigs, cats, and rats, and effects on blood gases in rats. Effects of exposure were also noted on susceptibility to respiratory infection. There were two phases in the guinea pig experiment: acute and chronic, defined according to exposure time. The acute phase exposed the experimental group to emissions for one hour per day, compared with 16 hours per day, 7 days per week, in the chronic phase. The concentration levels for emissions were the same for chronic and acute phases. Both phases began on November 15, 1976, and the chronic phase is to be completed March 25, 1977. Measurement of all animals, acute and chronic, is scheduled for completion by June 1977, and a final report is anticipated by October 1977.

The experiment investigating effects of inhalation exposure to catalyst-treated exhaust using cats, focused on pulmonary function and histopathology. Cats, being larger animals, allowed a wider range of pulmonary function tests, and using a variety of species of animals lends greater accuracy in extrapolating the data to humans. Measurements are to be completed by April 1977, and the report is to be prepared later in 1977.

Effects of exposure on arterial blood gases and pulmonary function were examined in rats. Rats were exposed to catalyst-treated exhaust 16 hours per day for 45 or 90 days, and parameters included body weight, food intake, lung weight, static lung compliance, and other respiratory function parameters and blood chemistry. Analysis of these data is scheduled for completion in 1977.

Difference in susceptibility to respiratory infection as a result of exposure to catalyst-treated exhaust were examined against the hypothesis that exhaust exposure will enhance susceptibility to lethal infection and thus increase mortality in the exposed group. Principal variables in the experimental design were: type of exhaust, exposure duration, single versus intermittent infectious aerosol exposure, and animal age. Preliminary results support the hypothesis. Final analysis and reporting will be completed during 1977.

3. Automotive Diesel Emissions Studies

One of the concerns of CRP focuses on health hazards from diesel engine exhaust. There are increasing numbers of diesel-powered vehicles on the highways, and the EPA has been characterizing their exhaust components. To date it appears that although there are lower concentrations of carbon monoxide and hydrocarbons than from gasoline engines, there are higher concentrations of nitrogen oxides in diesel emissions. Diesel emissions are more visible to the public and particulate emissions are 20-50 times higher than gasoline-fueled cars burning unleaded fuel. Little biological information is available on diesel particulate deposits in the lung, and this is a major area of emphasis in the CRP diesel study.

A capability to study diesel engine emissions was designed into the Center Hill Road Laboratory in Cincinnati. Installation and calibration of this hardware is progressing satisfactorily, and investigation of the effects of the exhaust on animals are to begin in 1977. These studies include pulmonary function, histopathology and blood chemistry, biochemical alterations in the lung, and effects on spontaneous locomotor activity. This will be the first HERL experiment in exposing animals to diesel exhaust. To date, there is very little information in the literature to serve as a guide for anticipating biological effects of diesel exhaust exposure. The Cincinnati laboratory has extensive experience in assessing lung changes and pulmonary function; therefore, this will be a major emphasis.

4. Ultrafine Sulfuric Acid and Metal Sulfates

Automobiles using catalytic converters emit ultrafine H_2SO_4 . Studies on the effects of exposure to H_2SO_4 have previously used H_2SO_4 particles beyond the size of the ultrafine range because development of a generation system for the proper size had not been completed. In the studies using the greater size H_2SO_4 particles (≥ 0.1 micrometers), the data suggest an increase in pulmonary resistance in animals exposed, but these are considered acute exposures. Little information is available on the effects of long-term low-level exposures. Along with projected studies of such exposures, the toxicity of some of the metal sulfates will also be determined.

5. Manganese Oxide Studies

The Federal requirement for phasedown of lead in gasoline, additive methylcyclopentadienyl manganese tricarbonyl (MMT), an organic manganese compound, was proposed as an alternate antiknock. The possible toxicity of airborne manganese subsequently became a concern of CRP, and inhalation exposure studies are scheduled for 1977. Parameters of major interest include pulmonary changes and neurological alterations.

Manganese is an element essential to life and in trace amounts is beneficial. When man is exposed to industrial amounts, two clinical syndromes are manifest: manganese pneumonia and manganese

poisoning affecting the central nervous system (CNS). The CRP in HERL/Cincinnati have designed studies to examine changes in the lung and CNS effects, and to investigate retention, tissue distribution, and excretion following acute inhalation exposure to $^{54}\text{MnSO}_4$ and $^{54}\text{Mn}_2\text{SO}_3$ aerosols.

D. Health Effects Research Laboratory/Research Triangle Park

Catalyst Research Program (CRP) activities performed by the Health Effects Research Laboratory (HERL/RTP) can be divided into three major areas of research: studies on sulfuric acid, studies on metals, and characterization of in-use catalyst vehicle emissions. Discussion of each project appears in this volume in the HERL/RTP program report (Appendix D).

1. Sulfuric Acid Research

The CRP's interest in sulfuric acid (H_2SO_4) stemmed from the finding that the catalytic converter, used as an emission-control device in American cars since 1975, can produce significant sulfuric acid emissions. Animal studies during 1976 have focused on the effect of inhalation of sulfuric acid mist on the immune system. The lymphocytes of rabbits exposed to 1 mg/m^3 ($0.3 \text{ }\mu\text{m}$ - $0.5 \text{ }\mu\text{m}$ for 4 hours a day for 2 days) showed a marginally significant ($p < 0.1$) increase in transformation of T cells, suggesting the possibility that sulfuric acid enhanced the blastogenesis of T cells or caused an alteration in the ratio of B:T cells. (See Table 1 in the HERL/RTP laboratory report). A statistically significant ($p < 0.05$) decrease in hematocrit occurred after a single 2-hour exposure to the acid mist. The number and percent of polymorphonuclear leukocytes (PMN) increase ($p < 0.05$) and the number and percent of lymphocytes decreased ($p < 0.05$) both in the animals exposed to acid mist and in the controls exposed to air. The changes were greater ($p < 0.05$), however, in the acid-exposed animals, indicating that a nonspecific stress was enhanced by the sulfuric acid. The experiments also revealed a decrease ($p < 0.05$) in hematocrit following exposure to the aerosol. Table 3 in the HERL/RTP laboratory report, presents the hematocrit measurements.

One of the most interesting results of these experiments was the finding that when a 2-hour exposure to sulfuric acid (1.0 mg/m^3) was preceded by a 3-hour exposure to sulfuric acid (1.0 mg/m^3), the mortality increased significantly over that caused by either pollutant alone. This apparent additive effect suggests that exposure to ozone initiates changes in tissue resulting in increased sensitivity to sulfuric acid.

In addition to these animal studies on sulfuric acid, the CRP is initiating a project to investigate the health effects of low-level sulfuric acid aerosols on young healthy human male volunteers. This study

scheduled to begin early in 1977, will use sulfuric acid concentrations ranging from 50 to 200 $\mu\text{g}/\text{m}^3$ with a mass median diameter ranging from 0.05 μm to 0.5 μm in an attempt to reflect the projected sulfuric acid aerosol burden created by increased use of the catalytic converter. The test parameters will be primarily measurements of pulmonary function.

One vegetation study has been conducted as part of CRP's interest in sulfuric acid. The project at the University of Minnesota's Department of Plant Pathology has investigated the effects of submicro-metric sulfuric acid aerosol exposure on vegetation. Hybrid poplar, pinto bean, and soybean showed marginal and tip necrosis when exposed to 25-30 mg/m^3 sulfuric acid aerosol.

2. Metals Research

The metals research conducted in 1976 by HERL/RTP under the CRP focused on manganese (Mn) and platinum (Pt). Studies on manganese were performed in conjunction with a laboratory-induced streptococcal infection in order to determine the relationship between manganese inhalation and chronic respiratory disease in mice. A statistically significant enhancement in respiratory infections occurred after 2-hour inhalations of manganese at $\geq 2.0 \text{ mg Mn}/\text{m}^3$ for manganous-manganic oxide atmospheres (Mn_3O_4) and $\geq 3.2 \text{ mg Mn}/\text{m}^3$ for manganese chloride aerosols ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$). Exposed animals also experienced delayed clearance and an increase in growth of inhaled streptococci. (See Figures 3 and 4 in the HERL/RTP laboratory report).

Most of the platinum studies sponsored by HERL are nearing completion with final results expected in 1977 or early 1978. Preliminary results from several studies are suggesting some of the element's possible adverse effects. Although research has shown that platinum does not induce allergy, palladium, when complexed with albumin, will induce a delayed allergy which can be transferred via spleen cells from sensitive donors. Platinum sulfate has been characterized as a severe eye irritant and may also have some cytogenetic activity. Preliminary results of a study of the effects of trace metals on the central nervous system suggest that platinum sulfate has a moderately depressive effect on behavior. It has also been shown that, under laboratory conditions, platinum sulfate or potassium hexachloroplatinate, like mercury, can be methylated with methyl B_{12} .

Reports associated with HERL/RTP metal studies which are expected to be of particular value to researchers include: (1) a series of reports, expected in late 1977, evaluating analytical methods for measuring trace elements in biological matrices; and (2) a follow-up report to "Proceedings - Catalyst Research Program Platinum Research Review Conference." Since platinum had received little attention before the establishment of the CRP, this report should be very helpful to researchers in the field.

3. Characterization of In-Use Vehicles

A study of 49 in-use catalyst vehicles which is being conducted in cooperation with New York State's Department of Environmental Conservation has as its major objective the measurement of sulfate, particulate, and regulated emissions. Few of the vehicles meet all regulated emission standards. In general, the tests show low sulfate and high carbon monoxide emissions. In many cases, the test cars were found to have had the idle mixture adjusted, increasing the carbon monoxide values beyond the manufacturers' specifications. The results reveal that idle carbon monoxide concentration correlates with carbon monoxide mass emission data and that sulfate emissions are inversely related to carbon monoxide values. Carbon monoxide and HC emissions tend to increase with mileage, but no overall correlation of sulfate with mileage is presently apparent. Other conclusions reached thus far indicate (1) that air pumps increase sulfate production and aid the converter's decrease of carbon monoxide, (2) that large amounts of sulfur dioxide are purged from catalysts upon deceleration to idle when idle carbon monoxide is high, (3) that little particulate sulfate is emitted in idle periods for either high or low carbon monoxide conditions, and (4) that emissions vary markedly according to vehicle manufacturer.

E. Office of Mobile Source Air Pollution Control/Washington, D.C.

As hydrocarbon, carbon monoxide, and nitrogen emissions are controlled, various unregulated emissions may be altered. It is important that these pollutants be characterized to assure that control of regulated emissions does not create problems in other areas. The unregulated emissions discussed in the following paragraphs are sulfuric acid, hydrogen cyanide, ruthenium, ammonia, polynuclear aromatic hydrocarbons, and diesel particulates.

1. Sulfuric Acid

Oxidation catalysts in exhausts oxidize a portion of the emitted sulfur dioxide to sulfuric acid. Sulfur dioxide is formed in the exhaust by combustion of trace quantities of organic sulfur compounds in gasoline. Even if the oxidation catalyst converted all of the sulfur dioxide in the exhaust to sulfuric acid, the resultant contribution from vehicles would be less than 1 percent of the total sulfuric acid in the atmosphere. However, it is possible to have high localized levels of sulfuric acid along heavily traveled roads. Experiments have been conducted by Exxon, GM, Ford, and Chrysler to determine the effect of various parameters (catalyst composition) on sulfuric acid formation. Also, tests have been run using sulfuric acid traps which are chemical containers (mufflers or catalyst-like) placed in the exhaust system after the oxidation catalyst. Ford and GM conducted work in measuring roadside sulfuric acid levels.

Work during the past year confirmed earlier studies showing that exhaust oxygen levels are the most important single parameter affecting sulfuric acid emissions. Low oxygen levels (such as those found with 3-way catalyst cars) can result in sulfuric acid emission levels of under 5 mg/mi which is equivalent to levels found with non-catalyst cars. Limited test results so far show that high mileage oxidation catalyst vehicles generally have lower sulfuric acid emissions. The past year's roadside measurement tests of sulfuric acid showed levels far below those predicted by EPA air quality models. These lower level measurements, plus the possible reduction of sulfuric acid emissions at higher mileages, may result in these emissions being considered much less of an air quality problem than previously thought.

2. Hydrogen Cyanide

In early 1976, EPA found that vehicles using 3-way catalysts could produce hydrogen cyanide (HCN) under rich malfunction modes. Since Volvo and Saab were certifying 3-way catalyst systems for use in California in 1977, EPA had to make a rapid determination on the levels of HCN that would be acceptable from a health standpoint. EPA was concerned primarily about worst-case situations, i.e., localized levels that could occur in indoor parking garages and along heavily traveled roadways. The highest HCN emissions were observed under rich malfunction modes when carbon monoxide (CO) emissions were also highest. In the closed environment it was found that the adverse health effects from CO would overshadow possible adverse effects from HCN by more than two orders of magnitude. For the worst reasonably conceivable highway-type exposure, it was determined that the amount of HCN present would not have unacceptable health effects. Tests for HCN emissions using a variety of catalysts were conducted by GM, Ford, and Chrysler.

It has been found that oxidation catalyst cars emit far less HCN than non-catalyst cars even under malfunction conditions. HCN emissions from catalyst cars are currently not a problem; however, HCN measurements should be made on future emission control systems as they are developed.

3. Ruthenium

Ruthenium is being considered by several companies for use in catalysts because of its low cost and attractiveness for nitrogen oxide control. Since ruthenium oxides are considered to be very toxic, it appears that the use of ruthenium catalysts depends on there being no significant emission of their oxides. EPA is not currently in a position to quantify what levels, if any, of emissions of ruthenium or its oxides would be considered significant. EPA health effects studies are planned for investigation of the toxicity of ruthenium and ruthenium oxides.

4. Ammonia

Ammonia emissions have been known to occur with dual catalyst systems under rich operating conditions. Ammonia formed over the reduction catalyst is frequently reoxidized to NO over the oxidation catalyst. Incomplete oxidation of the ammonia over the oxidation catalyst, however, could result in significant ammonia emissions. A malfunction of the oxidation catalyst system (e.g., air pump failure) could have similar results. Ammonia can also be formed with 3-way catalyst systems. EPA is currently investigating possible adverse health effects from automotive ammonia emissions to include both entire air quality regions and localized situations such as parking garages and heavily traveled freeways. Ford, GM, and Exxon are running tests on ammonia emissions resulting from various types of catalysts.

Ammonia emissions may be significant from vehicles with 3-way catalysts but only under malfunction conditions. Ammonia emissions from vehicles equipped with oxidation catalysts do not appear significant under normal operating conditions. Currently, there is inadequate information to permit determination of the level of ammonia emissions that would be considered acceptable.

5. Polynuclear Aromatic Compounds

The polynuclear aromatic compounds (PNA's) are a group of multi-ring aromatic hydrocarbon compounds with very low volatility and high molecular weight and are of interest due to their carcinogenicity. About 90 percent of the total PNA's in the atmosphere come from stationary sources, and it is estimated that of the remainder, half come from mobile diesels and half from other motor vehicles. PNA compounds in automotive exhaust have been studied for some time. It has been found that post-1968 cars have about half the PNA emissions of pre-1968 models. Tests on prototype cars with advanced catalysts and thermal reactors indicate a reduction in PNA emissions by 95 percent or more compared to uncontrolled vehicles. Recent Volkswagen tests on PNA emissions in gasoline engine vehicle exhaust confirm earlier Exxon work which shows only 5 percent of PNA emissions in catalyst-equipped cars over those in non-catalyst cars. VW also reported that their studies overall showed extremely low levels of PNA concentrations in automobile exhaust emissions.

6. Diesel Particulate Emissions

Mobile sources contribute a small, but significant, part of total suspended particulates in ambient air. Prior to the introduction of unleaded fuel, automobiles contributed between 2 and 13 percent of the total suspended particulates in urban areas. As the use of unleaded fuels in catalyst-equipped vehicles displaces the use of leaded fuels, the automotive contribution to urban air total suspended particulates will

decrease to about 0.2 to 1.3 percent. The introduction of large numbers of light-duty diesels may reverse this trend; therefore, it is important to investigate the quantity of diesel particulates emitted.

The composition of light-duty diesel particulates has not been completely determined. A major constituent of the particulates is known to be elemental carbon which has the ability to sorb other compounds. Sorbed compounds that have been identified include SO_2 , sulfate, high molecular weight organic compounds, and PNA's.

Almost all of the work to obtain emission factors on light-duty diesels had been accomplished by EPA either through contract or in-house testing; little data have been provided by the automobile manufacturers. Tests conducted to date show very high particulate emissions from light-duty diesels; about 25 times the values obtained for gasoline vehicles equipped with catalysts. The particulates consist of elemental carbon as well as various hydrocarbon compounds and small quantities of sulfate. The health effects, if any, associated with these particulates have not been determined.

III. DISCUSSION OF PROGRAM HIGHLIGHTS

During calendar year 1976, the various laboratories of EPA involved in the CRP continued tests and studies on mobile gasoline engine exhaust emissions, various gasoline engine catalyst systems, and the health effects which exhaust emissions have on humans, animals, and vegetation. Some studies and testing programs were newly initiated in CY-76, and other efforts were continuations of those initiated in previous years. Because of the imminent introduction of large numbers of light-duty diesel vehicles to the highways of the United States, attention also began to focus on diesel particulate emission and its effects on health. Highlights of research conducted under CRP and results obtained during CY-76 are presented in the paragraphs which follow.

A. Sulfates

Sulfur dioxide is formed in vehicle exhaust systems by combustion of trace quantities of organic sulfur compounds in gasoline, and oxidation catalysts in the systems oxidize a portion of the sulfur dioxide to sulfuric acid. Work during the past year confirmed earlier studies showing that exhaust oxygen levels are the most important single parameter affecting sulfuric acid emissions. Low exhaust oxygen levels, such as those found with 3-way catalyst cars, can result in low sulfuric acid emissions (under 5 mg/mi). Limited test results so far show that high-mileage oxidation catalyst vehicles have even lower sulfuric acid emissions (approaching 1 mg/mi). Car manufacturers are continuing to run tests on catalyst vehicles as they accumulate mileage. During the past year, GM completed a major test-tract experiment measuring roadside sulfuric acid levels. Results showed levels far below those predicted by EPA air quality models. The roadside lower levels, combined with further reduction in sulfuric acid emissions at higher mileages, may result in sulfuric acid emissions being considered much less of an air quality problem than previously hypothesized.

The main objective of the Los Angeles Catalyst Study (LACS) is to develop data on mobile source-related pollutants in the air before and after the introduction in 1975 of the catalytic converter. Analysis of data collected in CY 76 indicates that the use of the catalytic converter and unleaded fuel has resulted in a 25 percent decrease in carbon monoxide, lead, and total suspended particulates, while the freeway contributions of sulfates have increased less than 10 percent.

Under the National Fuels Surveillance Network program, analyses of samples of commercial gasoline showed that unleaded gasoline in Southern California contained approximately twice the amount of sulfur as New York samples. The content of sulfur in all three grades of gasoline was consistently higher in Los Angeles than in San Francisco.

An in-roadway study, conducted in October 1976, showed that catalyst vehicles caused an increase in sulfur concentration levels over background sulfate of no more than $1 \mu\text{g}/\text{m}^3$. No larger scale study of sulfates is planned, but there are plans to investigate the effects on automobile occupants driving immediately behind a cluster of high-sulfate-emitting vehicles.

During the reporting period, studies were initiated which seek to assess the health effect(s) of exposure to sulfuric acid aerosols. None of the studies thus far, however, have used sulfuric acid aerosols in the ultrafine size range, from 0.01 - $0.02 \mu\text{m}$ mass median diameter (MMD), which, as reported in last year's CRP report, may be the size range of the sulfuric acid actually emitted by automobiles equipped with catalytic converters. The capability of generating such ultrafine aerosols should soon be achieved, however, and studies should be underway shortly. Plans are complete for a human studies experiment which will test the effects of sulfuric acid aerosol health parameters (primarily pulmonary) of healthy young male volunteers. The aerosol generated will contain sulfuric acid particles ranging from 0.05 to $0.5 \mu\text{m}$. Results of these tests will be available in the 1977 report.

The 1976 health effects studies of sulfuric acid have suggested several ways in which the pollutant having a larger MMD affects laboratory animals. Results of studies using a concentration of $1 \text{ mg}/\text{m}^3$ sulfuric acid (0.03 - $0.5 \mu\text{m}$) suggest that such exposure may enhance blastogenesis of T cells or cause alterations in the ratio of B:T cells. Exposure also resulted in a decrease in hematocrit, an increase in leucocytes, and a decrease in lymphocytes, which was greater than that experienced by controls. It was also found that prior exposure to ozone increased the effect of exposure to sulfuric acid. It seems likely that ozone initiates changes in the tissue, making it more sensitive to sulfuric acid.

B. Hydrogen Cyanide

In early 1976, EPA found that vehicles using a 3-way catalyst could produce hydrogen cyanide (HCN) under rich-malfunction modes. There was concern regarding the levels of HCN that would be acceptable from a health standpoint under worst-case situations, such as levels that could occur in indoor parking garages and along heavily traveled roadways. In the closed environment it was found that adverse effects from carbon monoxide would overshadow possible adverse effects from HCN by more than two orders of magnitude. For the worst possible highway exposure, it was determined that the amount of HCN present would not cause adverse health effects.

C. Manganese Oxide

An organic manganese compound, methylcyclopentadienyl manganese tricarbonyl (MMT), was proposed for widespread use as a substitute additive when Federal regulations required a phasedown of the use of lead antiknock agents in gasoline. Manganese in trace amounts is an element essential to life, but when man is exposed to very high levels, two clinical syndromes are manifest: manganese pneumonia and manganese poisoning affecting the central nervous system. A possible increase in airborne manganese resulting from exhaust emissions prompted EPA to design manganese sulfate and manganese oxide inhalation studies scheduled to begin in 1977.

D. Polynuclear Aromatic Compounds

The polynuclear aromatic compounds (PNA) are a group of multi-ring aromatic hydrocarbon compounds with very low volatility and high molecular weight which are of interest due to their possible carcinogenic effects. About 10 percent of the total PNA's in the atmosphere come from motor vehicles, diesel as well as gasoline-powered. PNA compounds have been studied for some time, and it has been found that post-1968 cars have about half the PNA emissions that pre-1968 models have. Tests on prototype cars with advanced catalysts and thermal reactors indicate a reduction in PNA emissions by 95 percent or more compared to non-catalyst vehicles.

E. Ammonia

Ammonia emissions have been known to occur with dual and 3-way catalyst systems under malfunction operating conditions. Currently there is inadequate information on which to base a determination of the level of ammonia emissions that would be considered acceptable. EPA is now investigating possible adverse health effects from automotive ammonia emissions to include both entire air quality regions and localized situations, such as parking garages and heavily traveled freeways. Elements of the automotive industry are running tests on ammonia emissions resulting from various types of catalysts.

F. Ruthenium

Because of its low cost and attractiveness for nitrogen oxide control, ruthenium is being considered by several companies for use in catalysts. Since ruthenium oxides may be very toxic, the use of ruthenium in catalysts depends on there being no significant emission of its oxides. EPA plans to address the subject of toxicity of ruthenium and its oxides since EPA is not at this time in a position to quantify what levels of their emissions would be considered significant.

G. Platinum

Platinum studies have formed an important part of CRP's research program because the metal is commonly used in the catalytic converters for U.S. automobiles. The degree of emphasis on platinum is declining, however, and most platinum and other noble metal research is scheduled for completion in the next 18 months. A report is planned as a follow-up to "Proceedings - Catalyst Research Program Platinum Research Review Conference" which was published in early 1976. Since platinum had received little attention before the establishment of the CRP, the report should be extremely useful to future researchers.

H. Diesel Emissions

Since automobile manufacturers have indicated an intention to increase production of diesel-powered automobiles, EPA has initiated studies of diesel exhaust in anticipation that it may be asked to evaluate the risks versus the benefits of this development. Tests conducted to date show very high particulate emissions from light-duty diesels--about 25 times the values obtained for catalyst-equipped gasoline vehicles. The composition of diesel particulates has not been completely determined. It is known that the particulates consist of elemental carbon as well as various hydrocarbon compounds and small quantities of sulfates. Diesel engines have lower emissions of carbon monoxide than gasoline engines but higher concentrations of nitrogen oxides.

Very little information is available on the health effects of diesel emissions. The major health effects effort is being conducted jointly by ESRL, EMSL, and HERL. This effort is providing basic background information prior to whole animal testing. Installation and calibration of hardware in the Cincinnati Health Effects Research Laboratory to obtain more information in this area has progressed satisfactorily, and tests on animals are scheduled to begin in 1977. The laboratory has extensive experience in assessing lung changes and pulmonary function, and the major emphasis of the tests will be in these areas.

I. Health Effects of Exposure to Whole Exhaust

A major research effort during late CY-76 was the initiation of a 3-month exposure of laboratory animals to automotive catalytic-treated exhaust. The study placed major emphasis on defining the effects of the exposure on pulmonary function. The exposure period has been completed, data are being analyzed, and the reports should be completed in CY-77. After completion of this study, there are no immediate plans for additional animal exposures to automotive catalytic emissions.

APPENDIX A

THIRD ANNUAL CATALYST RESEARCH PROGRAM REPORT

Prepared by

**Environmental Monitoring and Support Laboratory
Research Triangle Park, N.C. 27711**

**U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
HEALTH EFFECTS RESEARCH LABORATORY
RESEARCH TRIANGLE PARK, N.C. 27711**

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I. OVERVIEW

The Environmental Monitoring and Support Laboratory's involvement in the Catalyst Research Program focuses on three major areas. They are the fuels and fuels additives, the Los Angeles Catalyst Study (LACS), and quality assurance.

The National Fuels Surveillance Network (NFSN) annually analyzes approximately 3,000 commercially purchased samples of gasoline, motor oil, fuel oil, and fuel additives.

The LACS, a monitoring program, was established to assess the impact of pollutants emanating from catalyst-equipped vehicles on ambient air quality adjacent to a major freeway. A variety of pollutants is being monitored by both integrated and continuous methods.

The quality assurance activities provide for the routine audits of laboratory analysis, development and distribution of standard reference samples and materials, measurement method evaluation, and quality assurance guidelines.

II. BACKGROUND AND INTRODUCTION

The Catalyst Research Program, established in 1974 as an interdisciplinary research program, involves three areas of the Environmental Monitoring and Support Laboratory, Research Triangle Park (EMSL/RTP): fuel collection and analysis, monitoring, and quality assurance. Previous reports (1-5) have summarized EMSL's activities prior to 1976. This report summarizes all catalyst-related work performed by EMSL during or related to calendar year 1976.

In the following pages each of the three aforementioned interdisciplinary areas which pertains to EMSL will be discussed.

III. CURRENT STATUS

A. Fuel Collection and Analysis

The advent of the catalyst-equipped vehicle which requires the use of unleaded gasoline initiated the surveillance of motor vehicle gasoline. Initial interest focused on sulfur in gasoline as a possible contributor to atmospheric pollution from engine emissions. Next, attention was directed to lead and phosphorus content of unleaded gasoline -- known poisons to vehicle catalysts. Unleaded gasoline by definition has limited lead and phosphorus content, with an allowed maximum of 0.05 grams lead per U.S. gallon (g Pb/gal) and 0.005 grams phosphorus per U.S. gallon (g P/gal). Presently, interest has expanded beyond these areas to include consideration of aromatic content, manganese content and other factors.

During the period of this report with the assistance of the EPA Regional Offices, EMSL collected and analyzed approximately 3,000 commercially purchased samples of gasoline (premium, regular, leaded, and unleaded), motor oil, fuel oil, and fuel additives. In addition, 70 unleaded samples were collected from New York State in support of the ROADS Study, a micrometeorological study conducted by the New York State Department of Environmental Conservation. The analyses included those for more than one element, using both isotopic dilution spark source mass spectrometry (ID-SSMS) and instrumental neutron activation (INAA). Of the 3,000 samples, approximately 100 unleaded gasoline samples were collected in Southern California by contractor and analyzed specifically for sulfur (S), lead (Pb), manganese (Mn), and phosphorus (P). Additional measurements were made to characterize the fuel including viscosity measurement, Reid vapor pressure (RVP), aromatic content, and American Petroleum Institute (API) gravity. Table I lists the analytical techniques employed for these measurements. Fuel composition data are utilized by researchers for emission characterization, mass-balance models, surrogate projections, and by officials concerned with mobile source enforcement and control decisions.

Table II compares sulfur, lead, and aromatic content of gasoline sampled in Los Angeles and San Francisco in the summer of 1975, winter of 1975-76, and summer of 1976. The average sulfur content of unleaded gasoline ranges from 0.017 wt. %S in San Francisco to 0.034 wt. %S in Los Angeles. This is nearly double the level measured in 70 New York samples (6). The analyses of both the regular leaded and premium leaded gasoline grades collected in Los Angeles and San Francisco indicate higher sulfur content in Los Angeles. Aromatic content of gasoline is of importance to the refiner since higher aromatic content can increase the octane number of the gasoline. As organic metallic fuel additives are reduced, the addition of aromatics is one way to keep the octane number up and avoid the customer complaint of "spark knock." Note that aromatic content is higher in the summer than winter.

A related activity includes analytical method development for fuels analysis. During the year, two methods were developed: sulfur in gasoline using gas chromatography with a flame photometric detector (7) and phosphorus in gasoline using a graphite furnace screening method (8). Work has started on the analysis of BaP in diesel exhaust.

B. Monitoring -- The Los Angeles Catalyst Study

The impact of pollutant emissions from catalyst-equipped vehicles on the ambient air has been studied since June 1974 in West Los Angeles adjacent to the San Diego Freeway. The study area was chosen because of heavy traffic (approaching 200,000 cars per day), total sulfur emissions from stationary sources are relatively low compared to the rest of the nation, predominant perpendicular winds to the freeway, and California's stricter standards for automotive emissions have resulted in a larger percentage of catalyst-equipped cars on the highway. Additional details concerning the site and sampling methodologies are available elsewhere (1).

TABLE I
Analytical Methods

I. Available and Used

Fluorescent Indicator Adsorption	ASTM	D - 1319
DEPENTANIZATION	ASTM	D - 2001
API Gravity @ 60°F	ASTM	D - 287
Reid Vapor Pressure	ASTM	D - 323
DISTILLATION	ASTM	D - 86
Sulfur, Lamp	ASTM	D - 1266

II. Available - Slow and Tedious

Sulfur, Lamp	ASTM	D - 1266
Phosphorus, Colorimetric	ASTM	D - 3231
Lead, Gravimetric	ASTM	D - 526

III. Developed In-House

Lead, AAS	ASTM	D - 3237
Lead, FTK	ASTM	D - 3348
Sulfur, GC/FPD		
Phosphorus, AAS-HGA		
Manganese, AAS		

TABLE II

Content of Sulfur, Lead, and Aromatics of Gasoline Collected
in San Francisco and Los Angeles by Season

	Sulfur (Weight % S)			Lead (g Pb/gal)			Aromatics (%)		
	H1	Low	Avg	H1	Low	Avg	H1	Low	Avg
<u>San Francisco Basin</u>									
Premium:									
Summer 75	0.024	0.001	0.009	--*	--	--	--	--	--
Winter 75-76	0.021	0.002	0.014	3.670	1.180	2.277	37.4	18.6	28.4
Summer 76	--	--	--	--	--	--	--	--	--
Regular:									
Summer 75	0.094	0.003	0.035	--	--	--	--	--	--
Winter 75-76	0.081	0.007	0.035	1.970	0.420	1.331	32.8	23.9	27.1
Summer 76	0.077	0.016	0.042	3.360	0.600	2.056	34.7	25.7	28.9
No Lead:									
Summer 75	0.068	0.003	0.027	--	--	--	--	--	--
Winter 75-76	0.038	0.002	0.017	0.015	0.003	0.007	38.6	19.6	30.6
Summer 76	0.046	0.012	0.030	0.018	0.001	0.006	42.5	28.5	33.8
<u>Los Angeles Basin</u>									
Premium:									
Summer 75	0.062	0.002	0.024	--	--	--	--	--	--
Winter 75-76	0.107	0.018	0.043	3.830	0.790	2.237	34.8	23.4	28.8
Summer 76	--	--	--	--	--	--	--	--	--
Regular:									
Summer 75	0.090	0.033	0.051	--	--	--	--	--	--
Winter 75-76	0.145	0.006	0.052	2.050	0.370	1.259	32.7	23.3	27.4
Summer 76	0.143	0.029	0.066	2.810	0.520	1.487	35.4	23.7	31.0
No Lead:									
Summer 75	0.085	0.010	0.034	--	--	--	--	--	--
Winter 75-76	0.058	0.006	0.025	0.007	0.002	0.004	37.3	27.5	32.7
Summer 76	0.048	0.012	0.026	0.007	0.001	0.004	44.1	26.9	34.1

* "--" means no measurements taken

The main objective of the Los Angeles Catalyst Study (LACS) is to develop ambient air data bases for sulfate (SO_4), carbon monoxide (CO), lead (Pb), and other mobile source-related pollutants before and after introduction of the 1975-model automobiles that employ catalytic converters. The data from this study are being analyzed to determine whether the catalytic converter has significantly increased the ambient sulfate levels and/or simultaneously decreased the ambient CO and Pb levels near the San Diego Freeway in Los Angeles.

The Environmental Monitoring and Support Laboratory (EMSL) is responsible for all study-related functions including instrumentation, operation, sample analyses, quality control, and data validation and analyses. However, since January 1976, the operation of instruments and analyses of samplers were performed under contract to Rockwell International or by interagency agreement with the Lawrence Berkeley Laboratory. To assure the quality of the data supplied by these two organizations, EMSL maintains a comprehensive quality assurance program in all experimental aspects of the study (9). EMSL issues periodic reports which discuss the trends and the interrelationships among the various pollutant patterns (1-5). The LACS reports are available on request from the Office of the Director, EMSL/RTP.

The site locations in Los Angeles and the site layouts in relation to the San Diego Freeway are shown in Figure 1. By selecting sites with the prevailing wind perpendicular to the freeway, the cross-freeway contribution to the pollutant levels can be determined using concurrent upwind and downwind measurements.

Figure 2 is a horizontal-elevation view showing the vertical locations of the sites relative to the freeway. The monitoring equipment at each site also is indicated in the figure.

Three short-term studies have been performed at the LACS sites to determine: (1) the repeatability of 24-hour high volume sampler data, (2) the validity of utilizing data at upwind Site A for background levels, and (3) the repeatability and comparability of data from 4-hour high volume and membrane samplers. Results of the first two studies were included in earlier reports. The third study is contained with this report (Appendix I).

1. Data Analysis

a. Wind Data

The overall patterns of wind speed and direction are depicted in Figure 3. This figure, based on measured data at the site composited over the year, shows that the more prevalent wind directions and the higher wind speeds occur near the perpendicular direction to the

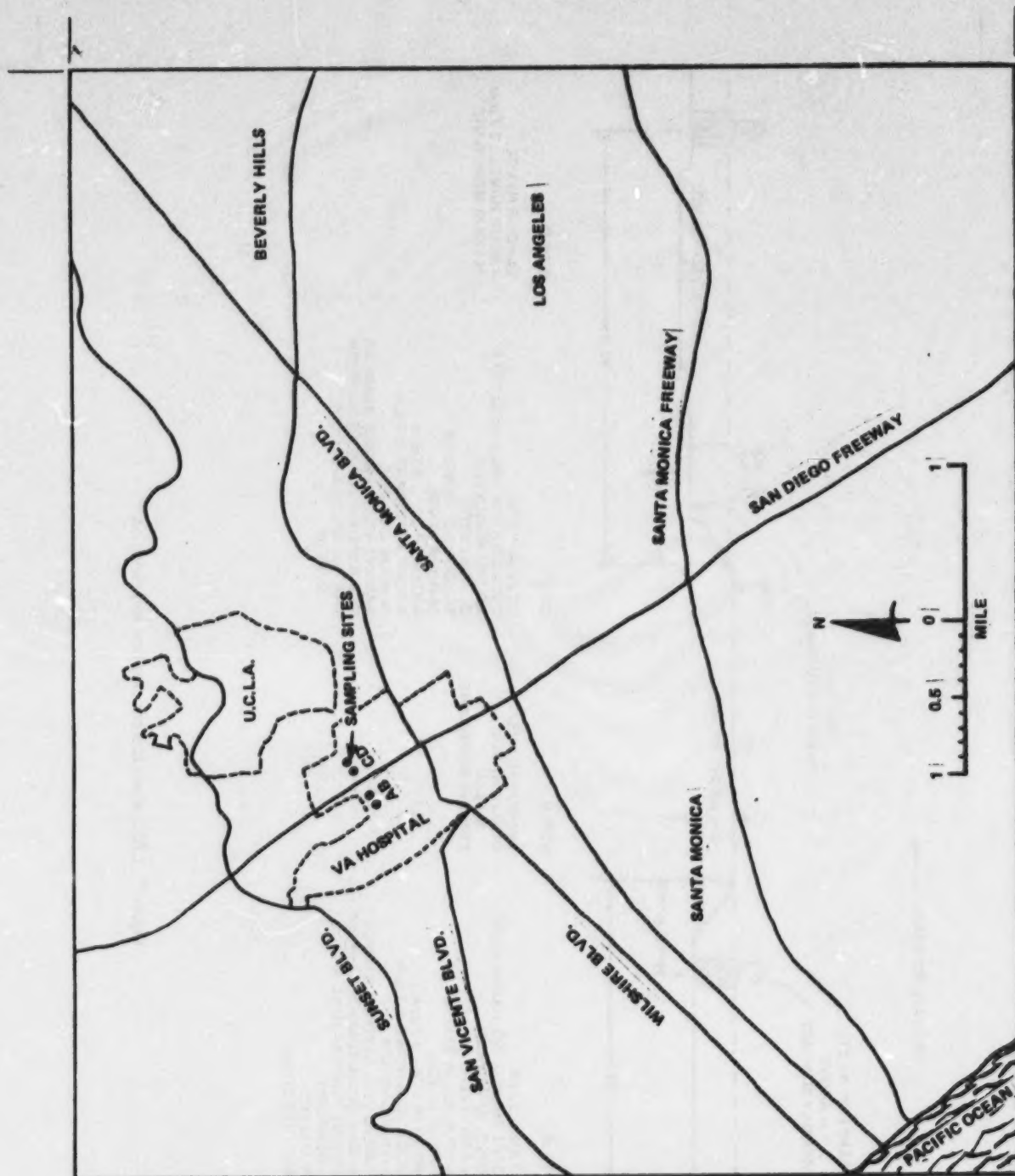


Figure 1. LACS site location in Los Angeles.

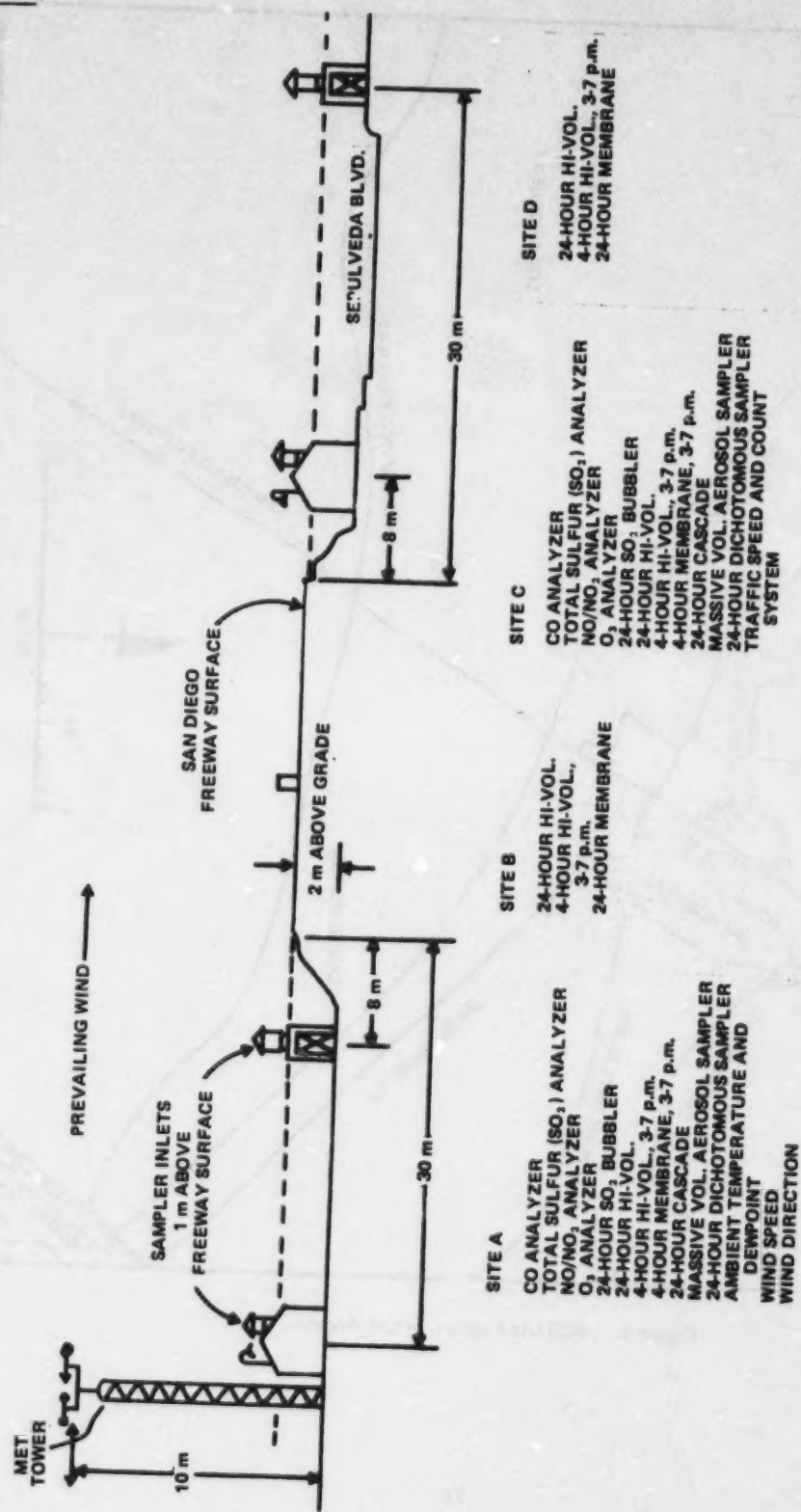


Figure 2. LACS study site composition and elevation.

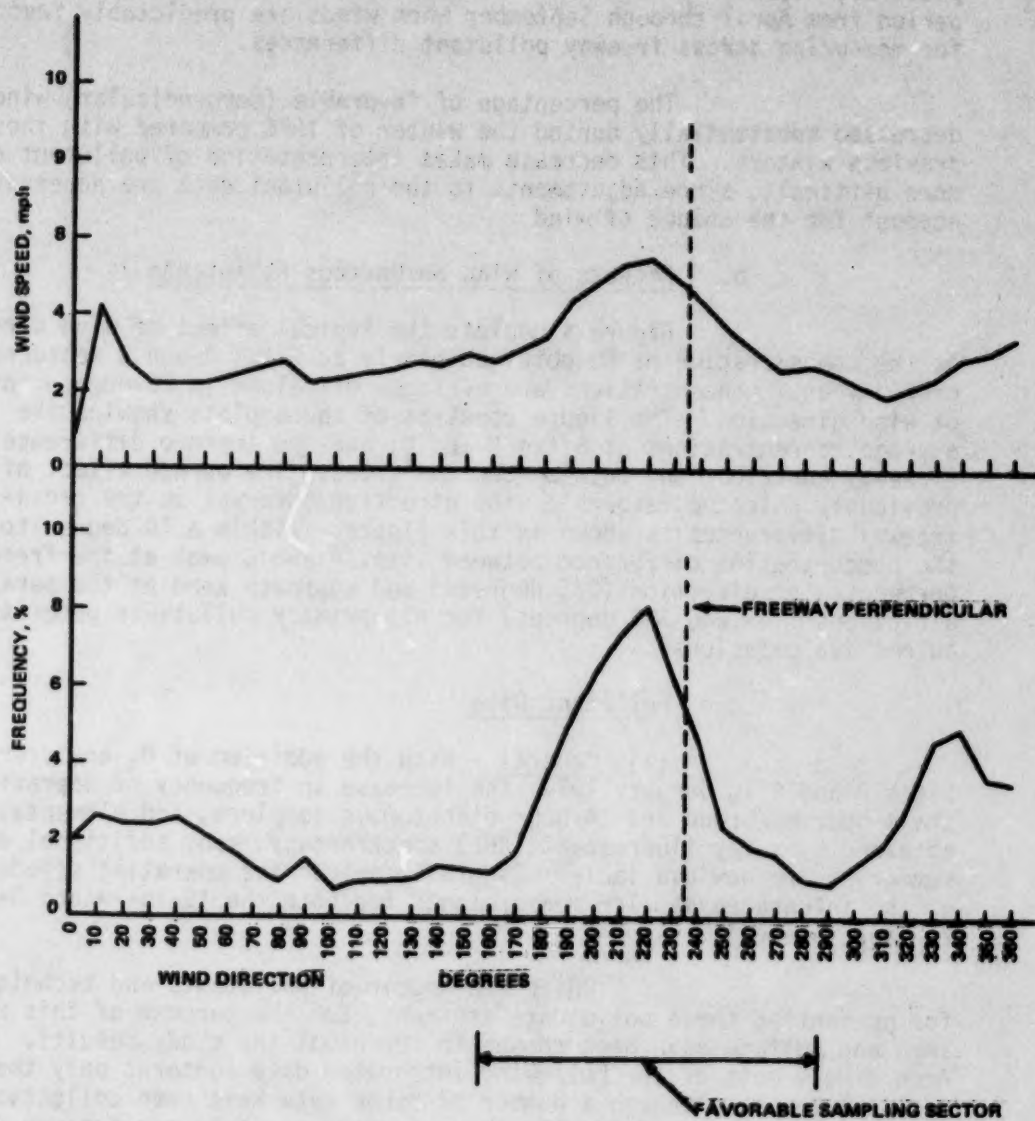


Figure 3. Annual wind frequency and speed by wind direction.

freeway. Micro-meteorology at the site tends to depict two distinct patterns, "summer" or "winter," with summer demonstrating a six-month period from April through September when winds are predictably favorable for measuring across freeway pollutant differences.

The percentage of favorable (perpendicular) wind decreased substantially during the winter of 1976 compared with those of previous winters. This decrease makes interpretation of pollutant data more difficult, since adjustments to the pollutant data are necessary to account for the change of wind.

b. Effects of Wind on Gaseous Pollutants

Figure 4 depicts the typical effect of wind direction on the concentration of CO obtained hourly at Sites A and C measured over a year. Concentrations are averages of values in 10-degree intervals of wind direction. The figure consists of three plots showing the average concentrations at Sites A and C, and the average difference (freeway contribution) between the two sites. The marked effect of the previously selected favorable wind direction interval on the cross-freeway differences is shown in this figure. Within a 10-degree tolerance, the concentration difference between Sites A and C peak at the freeway perpendicular direction (235 degrees) and approach zero at the parallel directions (145 and 325 degrees) for all primary pollutants generated by automotive emissions.

c. Pollutant Data

(1) General - With the addition of O₃ analyzers at Sites A and C in January 1976, the increase in frequency of operation of the 4-hour membrane and 24-hour dichotomous samplers, and elemental data obtained by x-ray fluorescent (XRF) spectroscopy, many additional data summaries are now available. Figure 5 depicts the operating schedules of the integrated sampler measurements for both the 15-to-19 and 0-to-24-hour intervals.

While the number of pollutants and techniques for presenting these pollutants are many, for the purpose of this report, lead and sulfate have been chosen to represent the study results. Accordingly most of the following integrated data concerns only these two pollutants, although a number of other data have been collected. Also the results are generally shown in figures as across-freeway differences -- Site C, Site A and the difference (C-A). Table III lists the parameters being monitored and the status of the data base. For more detail consult the references.

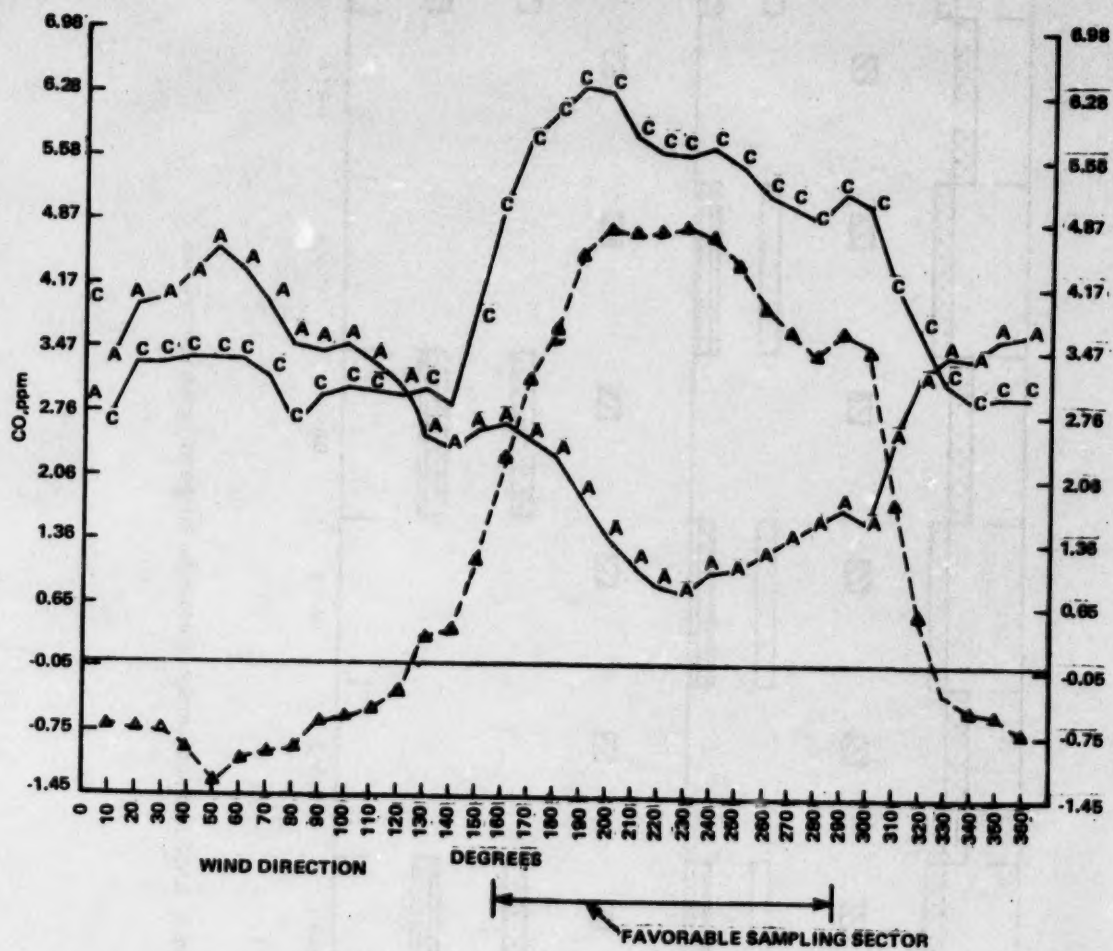


Figure 4. Carbon monoxide by wind direction, annual composite.

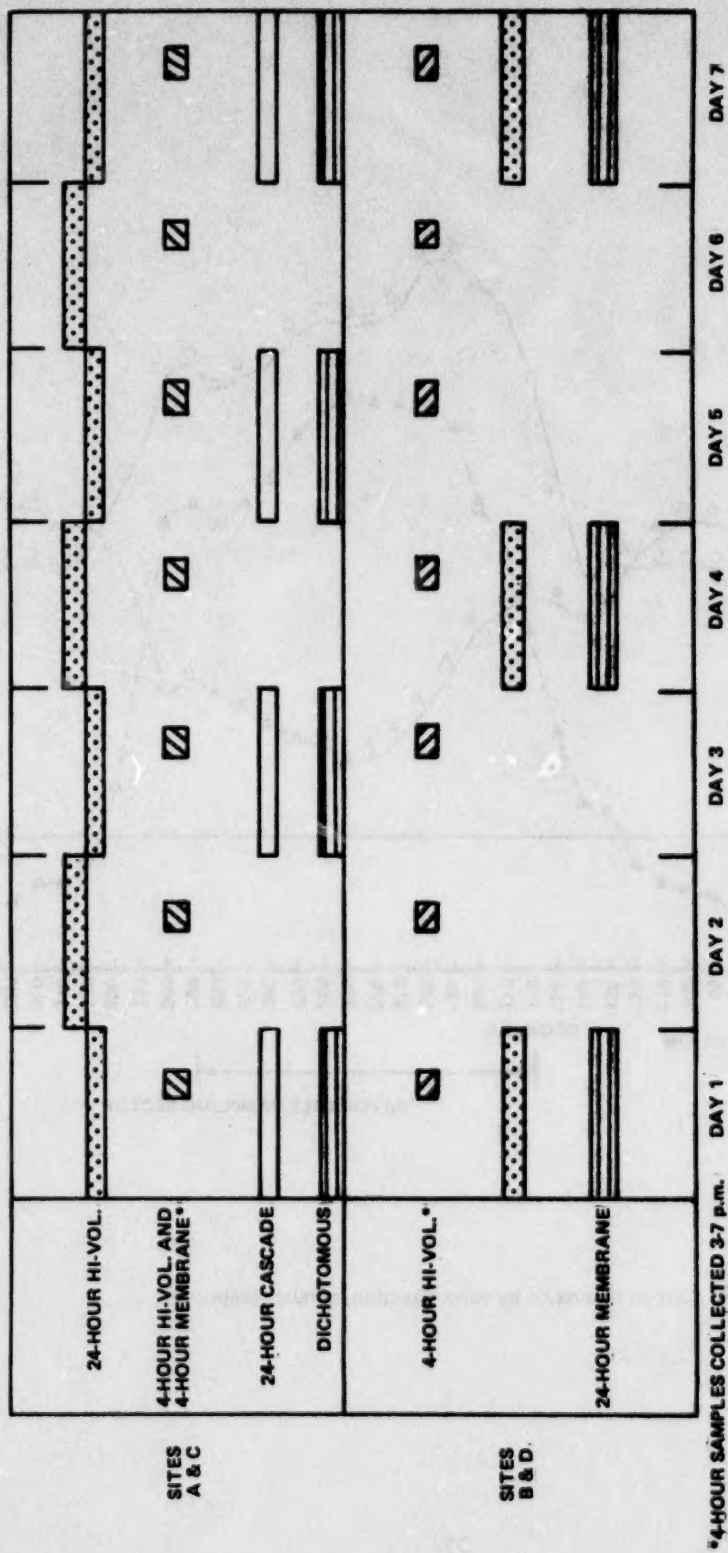


Figure 5. LACS platform sampler schedules for integrated sampling techniques.

TABLE III

Inventory of Integrated Data from LACS

Sampling Interval	Sampling Method	Sampling Sites	Sampling Frequency	Pollutants Determined	Sampling Period
6-10	Hi-Vol Membrane	B & D A & C	Every day Every 3rd day	TSP, Pb, SO ₄ ²⁻ , NO ₃ ⁻ TSP	6/74-12/74 6/74-12/74
8-12	Hi-Vol Membrane	B & D A & C	Every day Every 3rd day	TSP, Pb, SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ TSP, SO ₄ ²⁻ , NO ₃ ⁻ (XRF)*	1/75- 3/76 1/75- 3/76 7/75- 3/76
15-19	Hi-Vol	B & D	Every day	TSP, Pb, SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺	6/74-present
		A & C	Every day	TSP, Pb, SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺	1/75-present
	Membrane	A & C	Every 3rd day	TSP SO ₄ ²⁻ , NO ₃ ⁻ (XRF)*	3/75-present 9/74- 3/76 1/75- 3/76
			Every day	TSP, SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , (XRF)*	7/75- 3/76 3/76-present
0-24	Hi-Vol	A & C	Every day	TSP, Pb, SO ₄ ²⁻ , NO ₃ ⁻ NH ₄ ⁺	6/74-present 1/75-present
		B & D	Every 3rd day	TSP, Pb, SO ₄ ²⁻ , NO ₃ ⁻ NH ₄ ⁺	6/74-present 1/75-present
	Membrane	B & D	Every 3rd day	TSP SO ₄ ²⁻ , NO ₃ ⁻ (XRF)*	6/74-present 1/75-present 7/75-present
	Dichotomous Cascade (Backup)	A & C A & C	Every 2nd day Every 3rd day	NH ₄ ⁺ TSP, (XRF)*, strong acidity TSP	3/75-present 5/75-present 1/75-present
	Bubbler	A & C	Every day	(XRF)* SO ₂	7/75-present 6/74-present
Continu- ous	Climet Anemometer	A	Continuous	Wind direction/speed	6/74-present
	Thermistor/ LiCl Detector	A	Continuous	Temperature/dew point	10/74-present
	Inductive Loop System	All Lanes	Continuous	Traffic count/speed	9/76-present
	Non-Dispersive Infrared	A & C	Continuous	Carbon monoxide (CO)	6/74-present
	Chemiluminescence	A & C	Continuous	Nitric oxide (NO)/ Nitrogen dioxide (NO ₂)	1/75-present
	Chemiluminescence	A & C	Continuous	Ozone (O ₃)	1/76-present
	Flame Photometric	A & C	Continuous	Total sulfur (S)	5/75-present

*Elemental analyses by XRF include S, Pb, Br, Ca, Si, Fe, Zn, Al, and Cl.

(2) Four-Hour Integrated Sampler Data, 15-to-19-Hours

(a) High Volume Sampler Data. The 15-to-19-hour data from the samplers indicate that the average freeway contribution of total suspended particulate (TSP) between Sites A and C declined about 40 percent since the study began (25 percent from 1975 to 1976), although the background TSP (average $85 \mu\text{g}/\text{m}^3$) has not significantly changed. The freeway contribution of lead (Pb) during this period declined nearly 15 percent, although the background level (Site A) had not changed significantly (Figure 6). For example, the average lead difference in July 1975, was about $7.3 \mu\text{g}/\text{m}^3$ and the corresponding value in July 1976, was about 5.7, a drop of $1.6 \mu\text{g}/\text{m}^3$ ($\sim 20\%$).

The sulfate ($\text{SO}_4^{=}$) data from the high volume samplers (Figure 7) demonstrate that the average SO_4 background level (Site A) decreased more than 25 percent from the summer of 1975 to the summer of 1976. The SO_4 differences between Sites A and C in the summer of 1976 averaged only $2.8 \mu\text{g}/\text{m}^3$ as compared with $5.2 \mu\text{g}/\text{m}^3$ for a similar period in 1975. As a matter of interest, the SO_4 difference between Sites B and D, which operated daily like Sites A and C, remained essentially unchanged ($2.8 \mu\text{g}/\text{m}^3$ in 1975). The average values at Sites B and D also decreased more than 25 percent since the beginning of data collection in June 1974.

(b) Membrane Sampler Data. The membrane samplers use cellulose ester as the filter material as compared with glass fiber in the high volume sampler filters. For TSP, the 4-hour duplicate sample comparison study (10) indicated that the membrane and high volume sampler data exhibit a poorer correlation than was expected (~ 0.5). However, the 15-to-19-hour membrane sampler data for TSP exhibit a decrease in TSP background level similar to that indicated by the high volume sampler data. Although the monthly averages of the membrane sampler data indicate a wider fluctuation from month to month than did the high volume sampler data, the overall monthly average at Site A is identical by both types of samplers. At Site C, the high volume sampler levels of TSP were approximately 10 percent higher overall than the membrane sampler levels.

The 15-to-19-hour membrane sampler data for Pb shown in Figure 8 correlates well (0.99) with the 15-to-19-hour high volume sampler lead data. However, the membrane sampler data for Pb are approximately 20 percent higher than those determined by the high volume sampler. Monthly levels range as high as $11 \mu\text{g}/\text{m}^3$ at Site C which is about $1.5 \mu\text{g}/\text{m}^3$ higher than the maximum lead level by the high volume sampler.

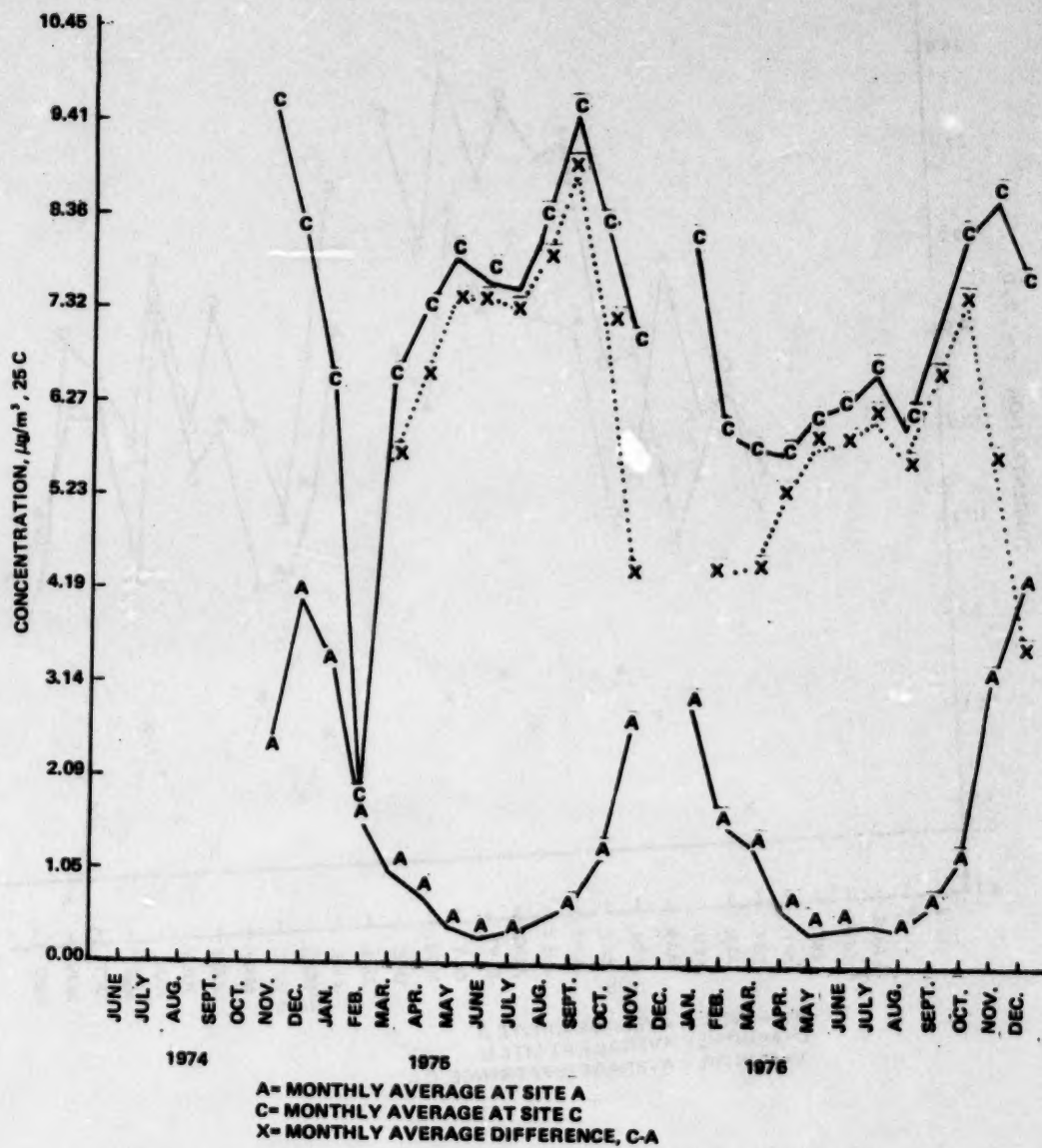


Figure 6. Monthly 4-hour lead from high-volume samplers.

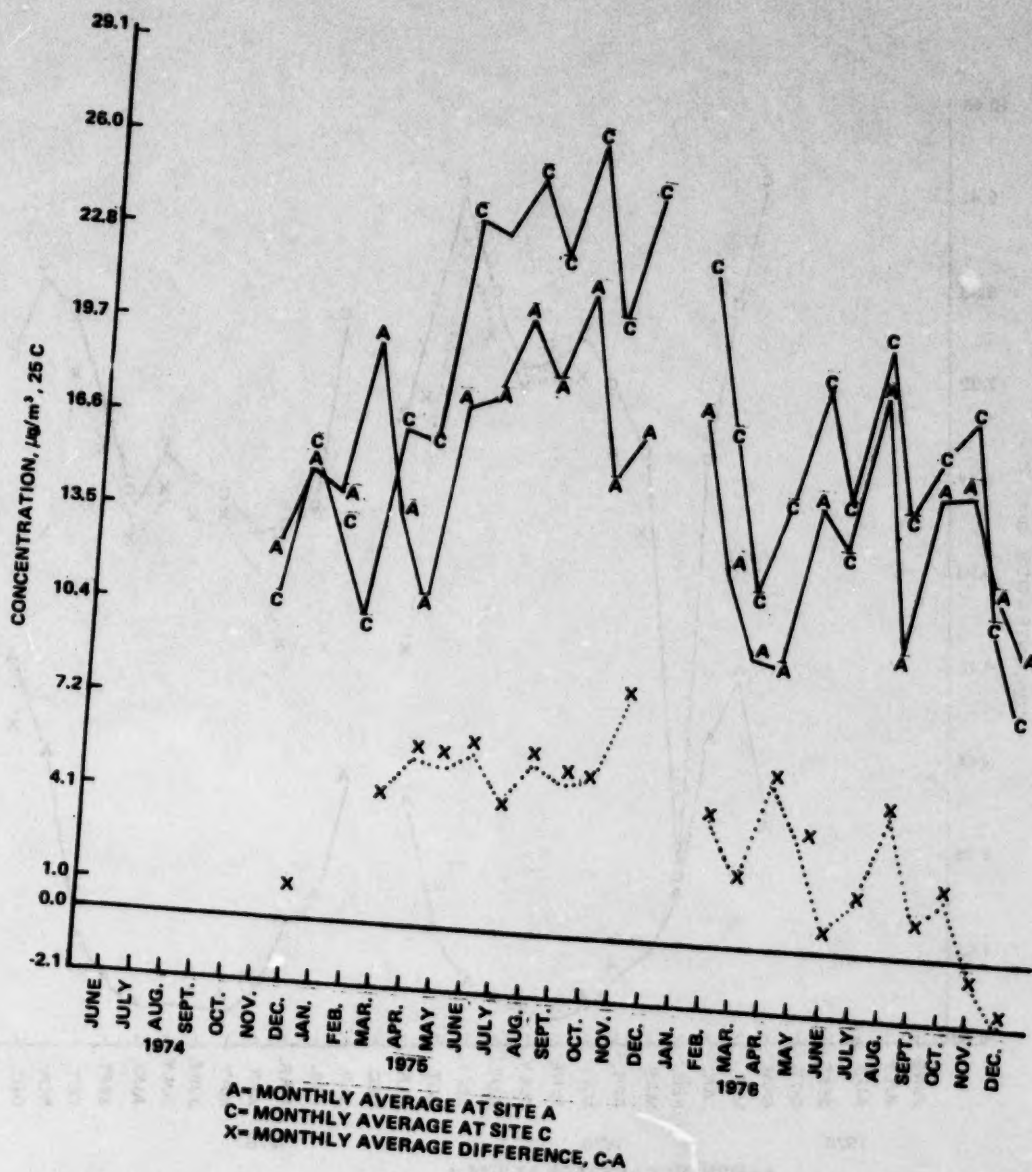


Figure 7. Monthly 4-hour sulfate from high-volume samplers.

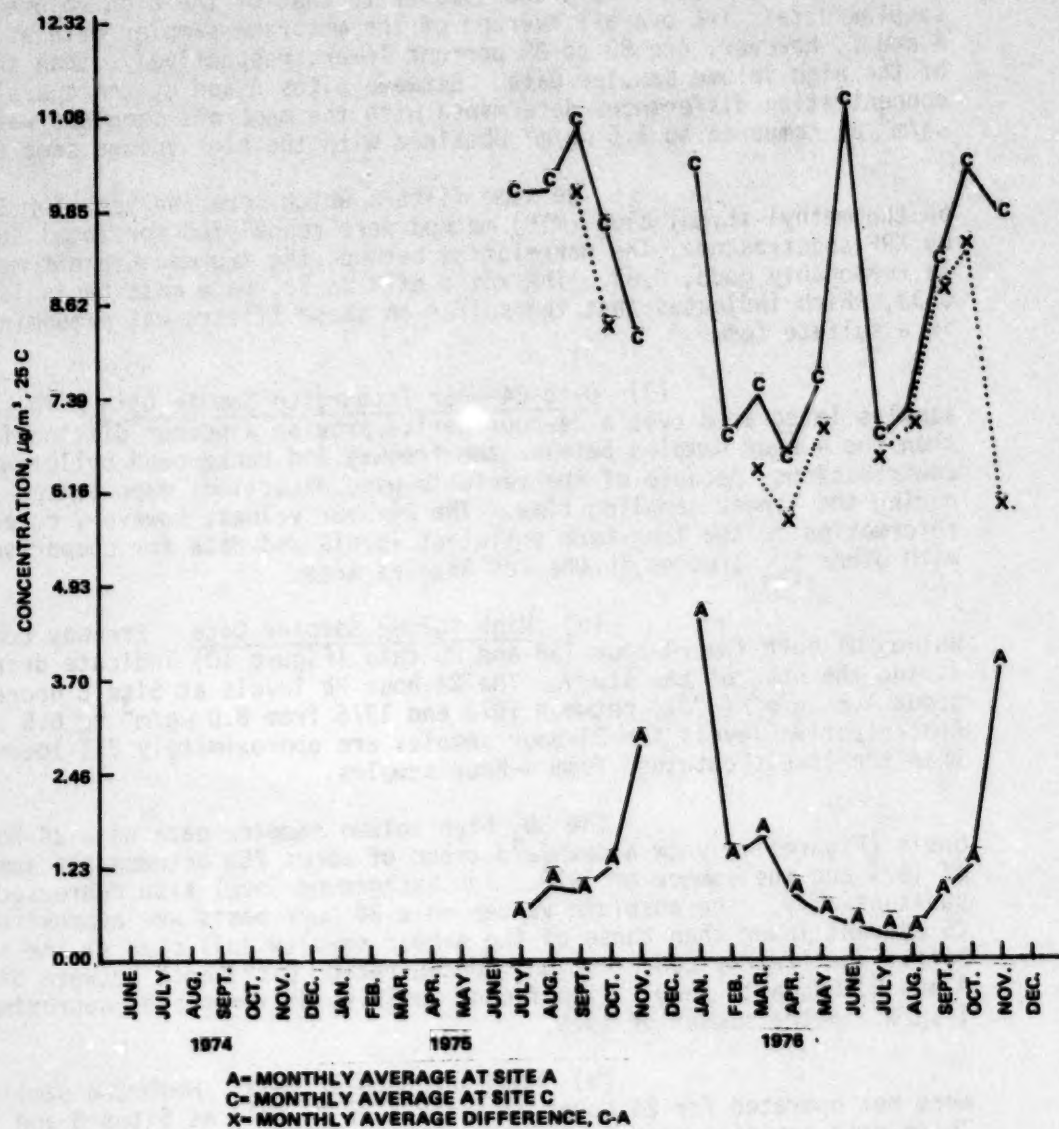


Figure 8. Monthly 4-hour lead from membrane filters.

The membrane sampler data for $\text{SO}_4^{=}$ (Figure 9) at Site A exhibit a downward trend similar to that of the high volume sampler data. The overall average of the membrane sampler data at Sites A and C, however, are 30 to 39 percent lower, respectively, than those of the high volume sampler data. Between Sites A and C, the overall concentration differences determined with the membrane samplers was $0.6 \mu\text{g}/\text{m}^3$ as compared to $3.5 \mu\text{g}/\text{m}^3$ obtained with the high volume samplers.

The same filters which were analyzed for $\text{SO}_4^{=}$ by the methyl thymol blue (MTB) method were reanalyzed for total sulfur by XRF spectroscopy. The correlation between the two measurement methods is reasonably good, 0.89. The ratio of S to SO_4 on a mass basis is 0.33, which indicates that the sulfur on these filters was predominately in a sulfate form.

(3) 0-to-24-Hour Integrated Sample Data - The LACS samples integrated over a 24-hour period provide a poorer distinction than the 4-hour samples between the freeway and background pollutant contributions, because of the variable wind directions experienced during the longer sampling time. The 24-hour values, however, do provide information on the long-term pollutant levels and data for comparison with other SO_4 studies in the Los Angeles area.

(a) High Volume Sampler Data. Freeway contribution of both the 24-hour TSP and Pb data (Figure 10) indicate decreases during the span of the study. The 24-hour Pb levels at Site C decreased about $1.5 \mu\text{g}/\text{m}^3$ (~20%) between 1975 and 1976 from $8.0 \mu\text{g}/\text{m}^3$ to $6.5 \mu\text{g}/\text{m}^3$. Concentration levels for 24-hour samples are approximately 25% lower than the levels obtained from 4-hour samples.

The $\text{SO}_4^{=}$ high volume sampler data on a 24-hour basis (Figure 11) show a downward trend of about 25% between the summer of 1975 and the summer of 1976. The background level also decreased substantially. The absolute values on a 24-hour basis are approximately 25 percent lower than those of the 4-hour samples collected at the same site. The freeway contribution (concentration difference between Sites A and C) began to show a significant positive difference of approximately $1 \mu\text{g}/\text{m}^3$ in the summer of 1976.

(b) Membrane Sampler Data. Membrane samplers were not operated for 24 hours at Sites A or C, only at Sites B and D. These data are discussed in another report (11).

(c) Dichotomous Sampler Data. The dichotomous samplers exhibited aerosol collection problems in the larger particle ranges and are not reported, but this caused no major problems to the

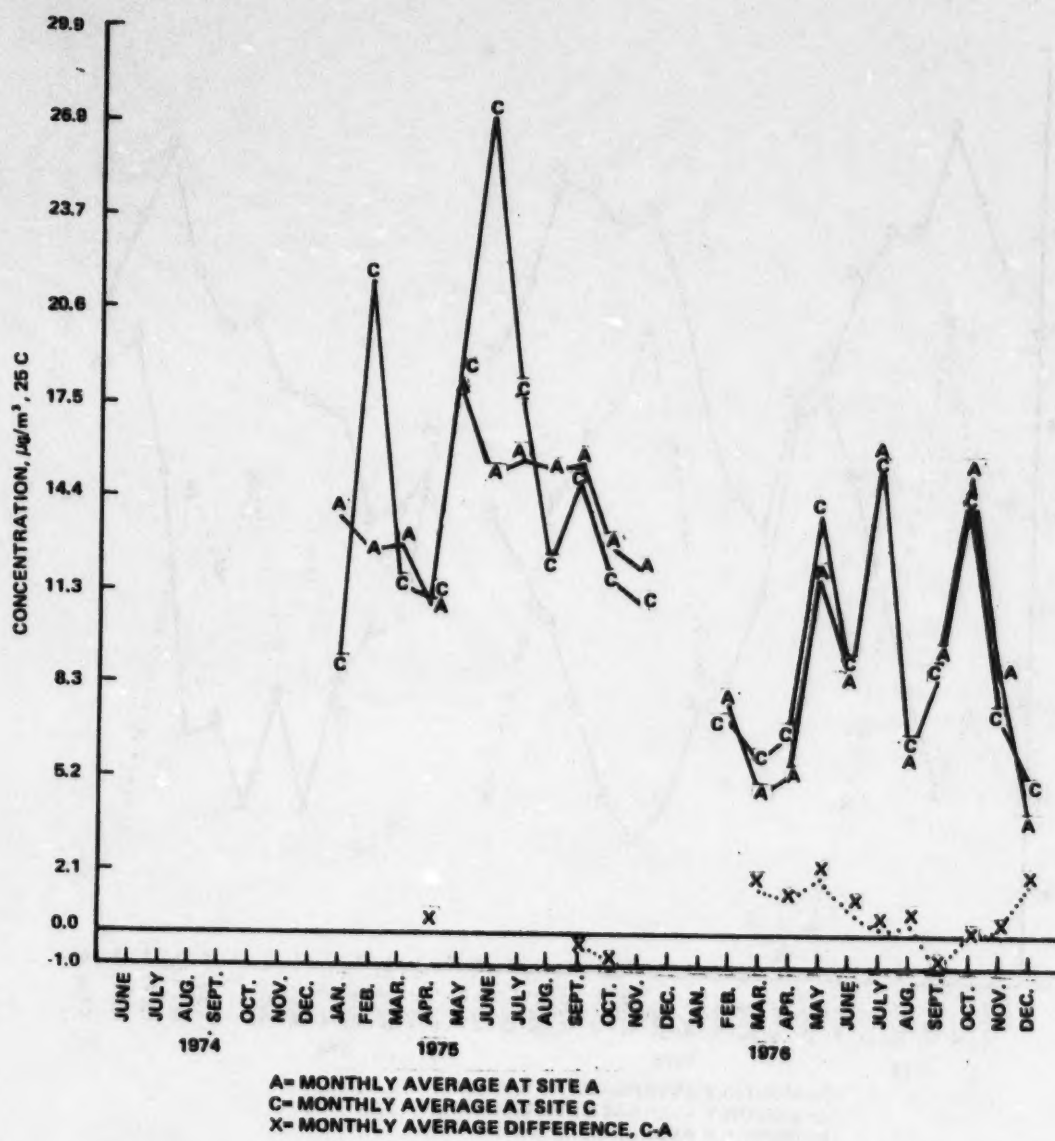


Figure 9. Monthly 4-hour sulfate from membrane filters.

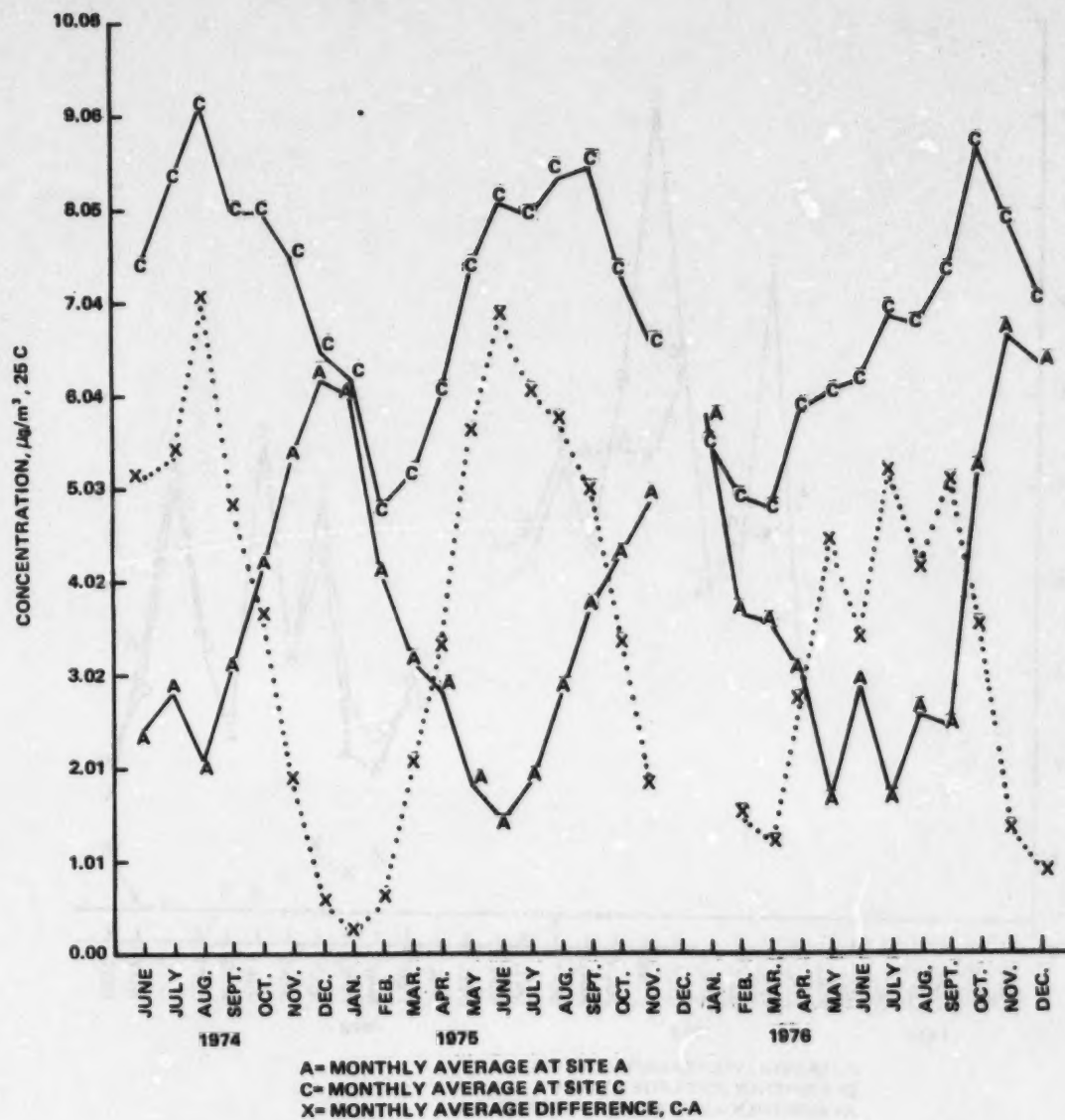


Figure 10. Monthly 24-hour lead from high-volume samplers.

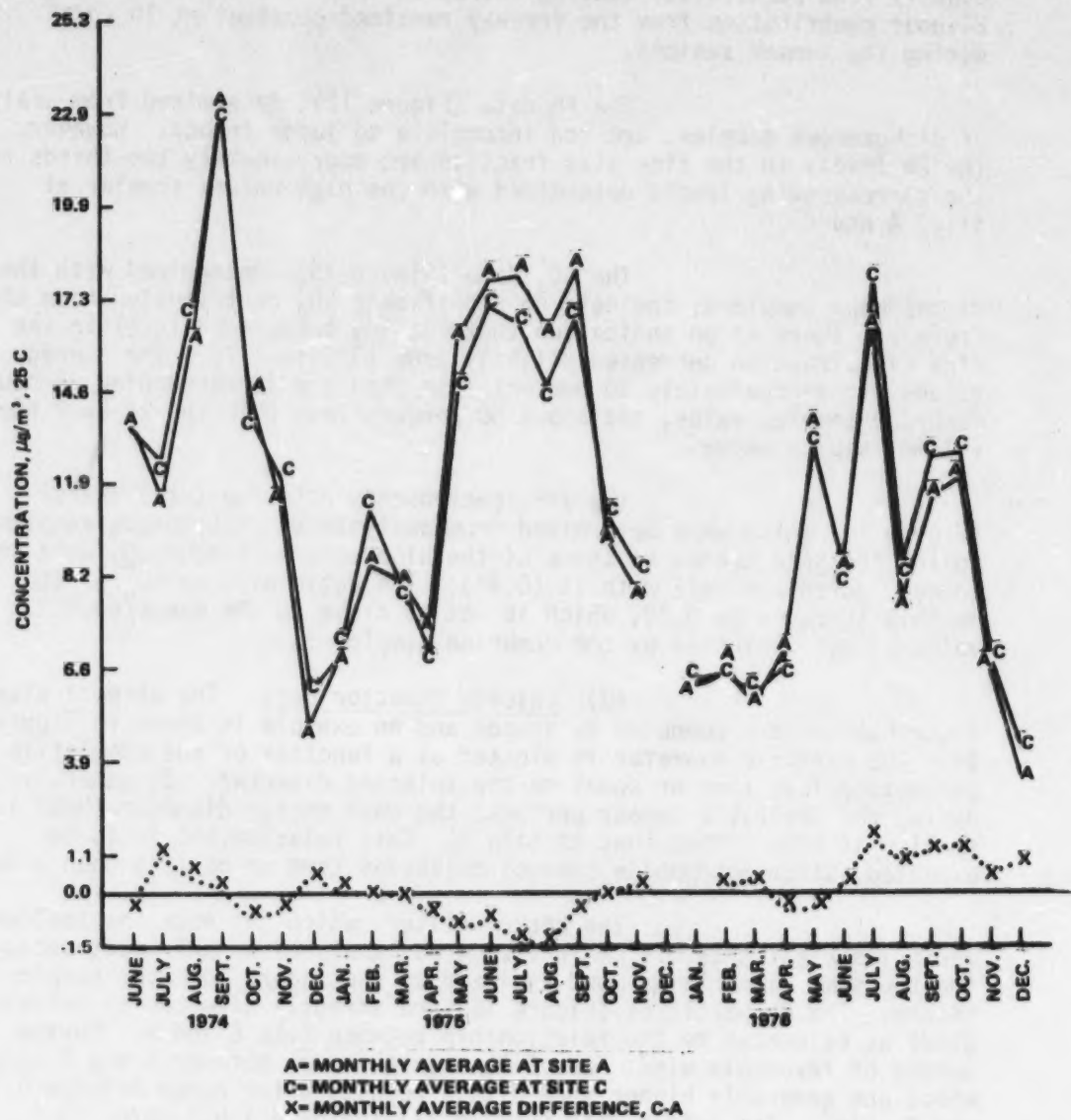


Figure 11. Monthly 24-hour sulfate from high-volume samplers.

study since the compounds of interest are primarily located in the small size range ($<2.5 \mu\text{m}$). The mass concentration data indicate that the overall fine particulate loading decreased from 1975 to 1976, and the 24-hour contribution from the freeway remained constant at $10 \mu\text{g}/\text{m}^3$ during the summer seasons.

The Pb data (Figure 12), determined from analysis of dichotomous samples, are too incomplete to judge trends. However, the Pb levels in the fine size fraction are approximately two-thirds of the corresponding levels determined with the high volume sampler at Sites A and C.

The $\text{SO}_4^{=}$ data (Figure 13), determined with the dichotomous samplers, indicate no significant SO_4 contribution from the freeway. There is an indication that the SO_4 background level in the fine size fraction decreased slightly from 1975 to 1976. The average values are approximately 30 percent less than the corresponding 24-hour membrane sampler value, and about 60 percent less than the 24-hour high volume sampler values.

The XRF spectroscopy data for total sulfur (Figure 14) which were determined from analysis of dichotomous samples, follow the same trends as those of the high volume 24-hour SO_4 data and, indeed, correlate well with it (0.95). The ratio of S to SO_4 of the monthly averages is 0.28, which is not as close to the expected 0.33 value as was exhibited by the membrane sampler data.

(d) Cascade Impactor Data. The aerosol size distributions are computed by season and an example is shown in Figure 15. The particle diameter is plotted as a function of the cumulative percentage less than or equal to the selected diameter. In general, during the favorable summer periods, the mass median diameter (MMD) is smaller at Site C than that at Site A. This relationship is to be expected, since automobile aerosol emissions tend to be less than $1 \mu\text{m}$ in size.

The backup filter, which collects the smallest particles (less than $0.7 \mu\text{m}$ in size), was analyzed by XRF spectroscopy for the same elements as were analyzed on a standard membrane sampler filter. The Pb particles (Figure 16) are strongly affected by unfavorable winds as evidenced by the relationship between Site C and A. During 3 months of favorable wind, Site C Pb results range between 4 and $6 \mu\text{g}/\text{m}^3$ which are generally higher than Site A results which range between 0.5 and $4 \mu\text{g}/\text{m}^3$. The sulfur data (Figure 17) indicate a $0.2 \mu\text{g}/\text{m}^3$ ($0.6 \mu\text{g}/\text{m}^3$ equivalent SO_4) contribution from the freeway traffic during the summer seasons in 1975 and 1976.

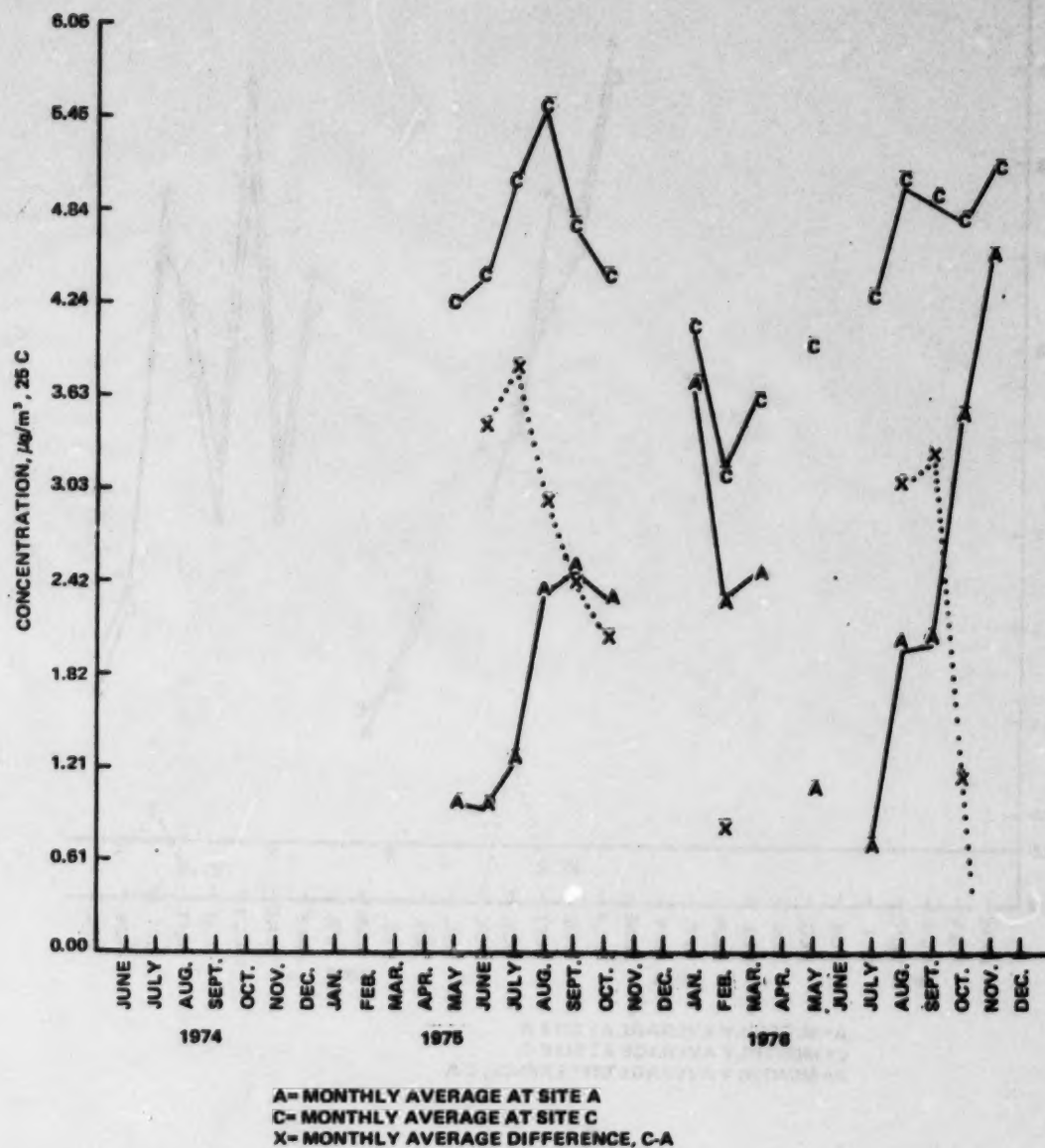


Figure 12. Monthly 24-hour lead from dichotomous samplers.

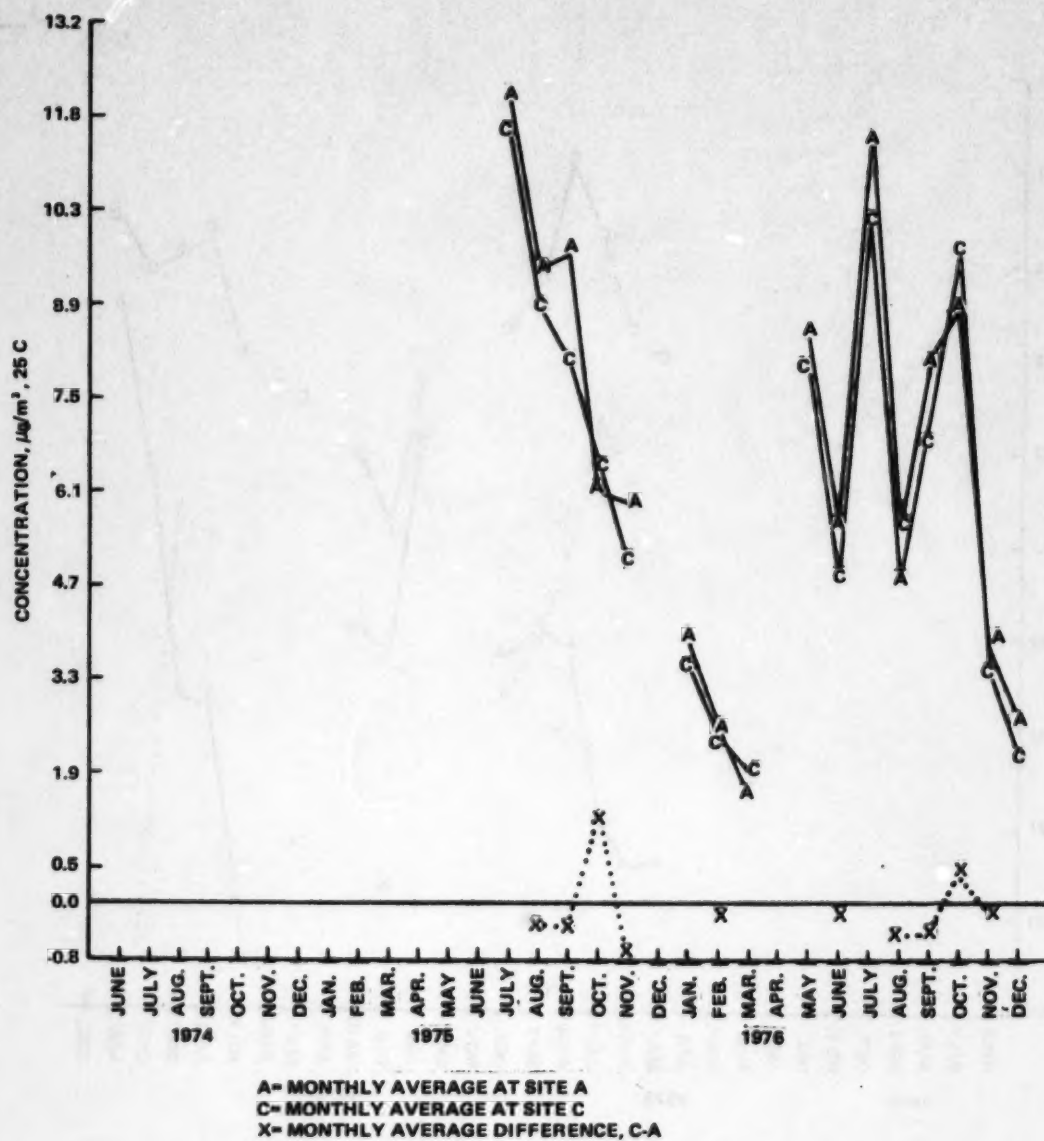


Figure 13. Monthly 24-hour sulfate from dichotomous samplers.

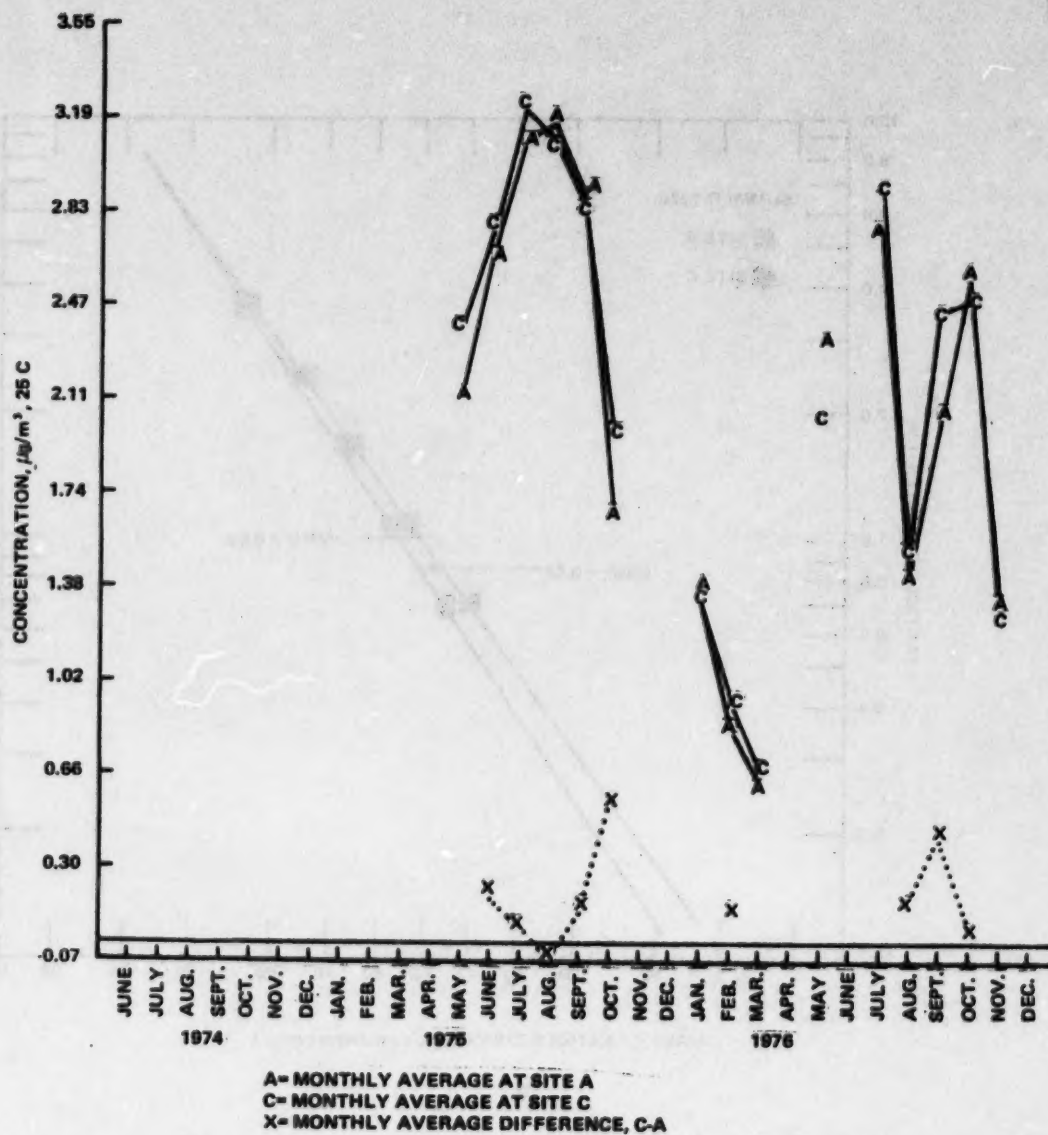


Figure 14. Monthly 24-hour total sulfur from dichotomous samplers.

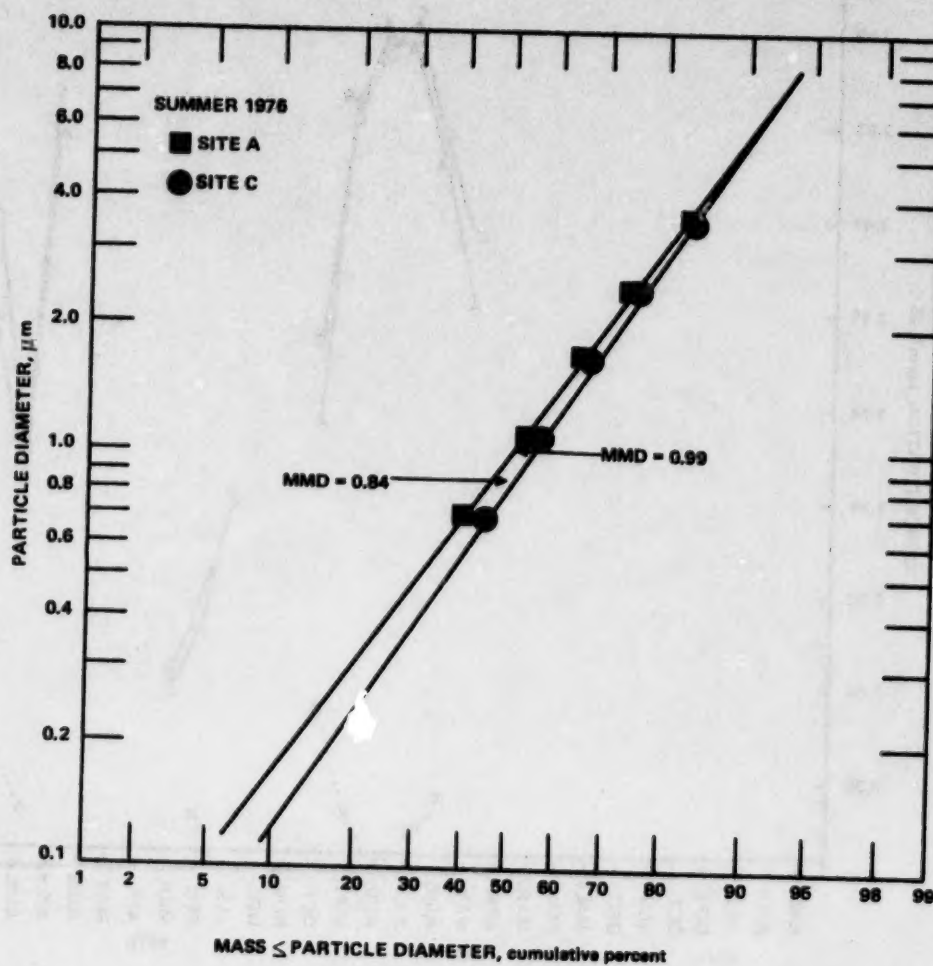


Figure 15. Cascade impactor results for summer 1976, by site.

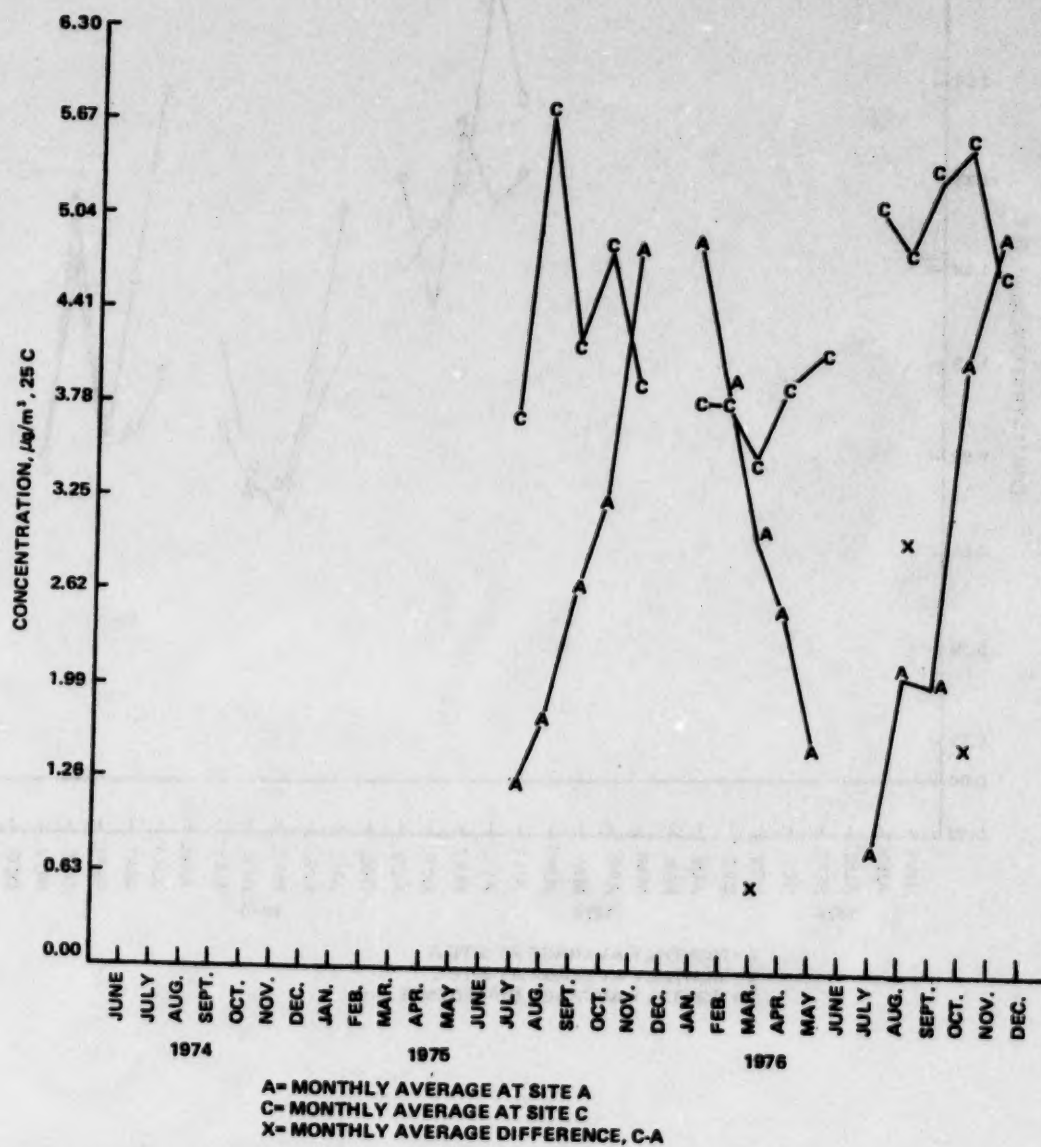


Figure 16. Monthly 24-hour lead particles $\leq 0.7 \mu\text{m}$ as determined by cascade impactor.

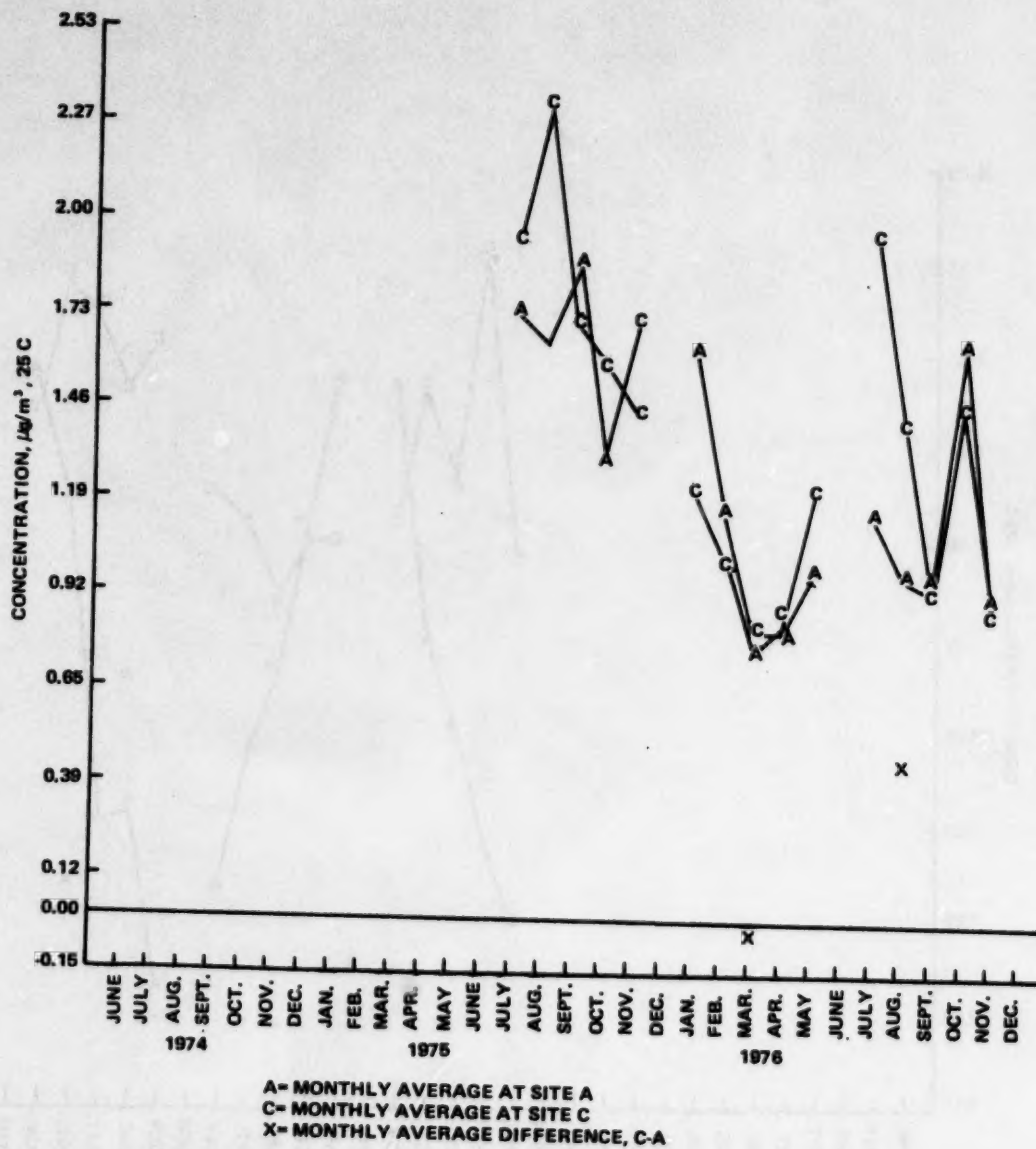


Figure 17. Monthly 24-hour sulfur particles $\leq 0.7 \mu\text{m}$ as determined by cascade impactor.

To examine the distribution of $\text{SO}_4^{=}$ and Pb across the cascade size range, composite analyses were performed combining stages for a number of samples. To minimize the sample size, 35 cascade sets in which all six stages contained valid data were selected from the data for each of Sites A and C for the summer of 1975. From the analyses of these samples, weighted averages were calculated. From these data, cumulative percentages were determined and size distributions were plotted.

The Pb data (Figure 18) indicate similar distributions at both sites, but the particles collected at Site C were smaller than those obtained at Site A. The plots of $\text{SO}_4^{=}$ data (Figure 19) collected at both sites again indicate a similar curvature as that determined previously and, within the experimental uncertainty of the method, do not indicate a difference in median size.

(e) SO_2 Bubbler Sampler Data. Figure 20 presents 24-hour SO_2 data obtained with bubbler samplers and indicates that a significant change did not occur in the SO_2 background level and only a slight decrease was experienced in the freeway contribution. Few monthly averages exceed $26 \mu\text{g}/\text{m}^3$.

(4) Hourly Averages of Continuous Data - Hourly averages were derived from measurements of the pollutants -- CO , NO , NO_2 , O_3 , and total sulfur -- and the ancillary measurements of wind speed and direction, ambient temperature and relative humidity, and traffic count and speed in each lane. The wind data have already been discussed.

(a) Pollutant Data. The summary data by month for the continuously monitored pollutants are presented in Figures 21 through 25. Because of the interrelationship between the wind and pollutants, the pollutant data were analyzed according to the two seasons, winter and summer.

The CO plot indicates no apparent change in background level, but a decrease of approximately 20 percent in the cross-freeway difference between Sites A and C from the summer of 1975 to the summer of 1976. The NO data shown in Figure 22 is difficult to interpret because of the erratic nature of the plot, but the dramatic increase of NO at Site C in September 1976 is apparent and unexplainable. According to quality control records, the instrument used to monitor for NO was operating properly during this month. In Figure 23, the NO_2 data collected at Site C during September also shows a similar peak, but neither the CO nor the O_3 data (Figure 25) suggest any reason for the peak readings. The NO_2 plot is also erratic and somewhat difficult to

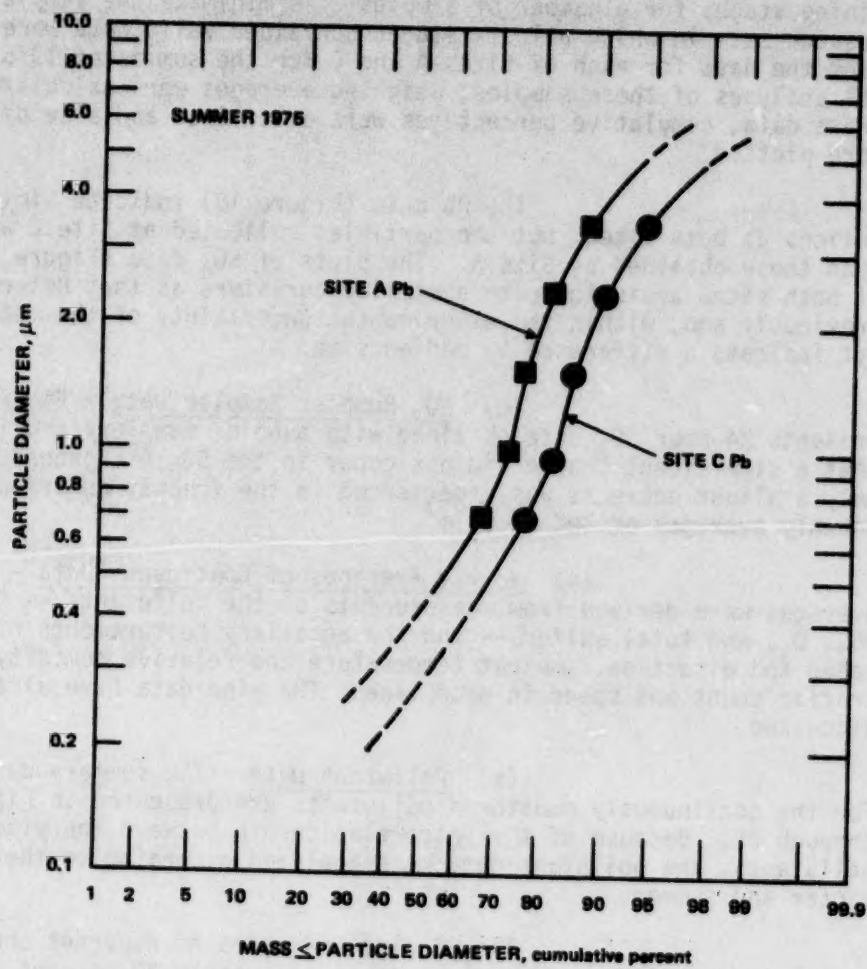


Figure 18. 24-hour cascade composites, lead.

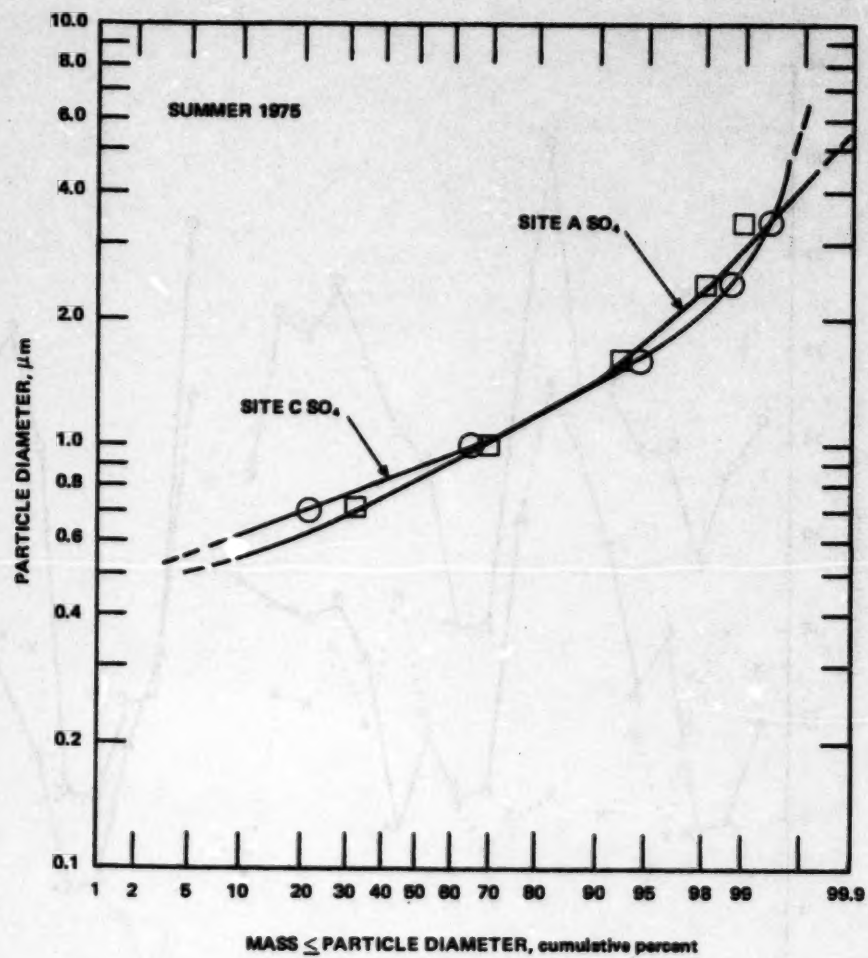


Figure 19. 24-hour cascade composites, sulfate.

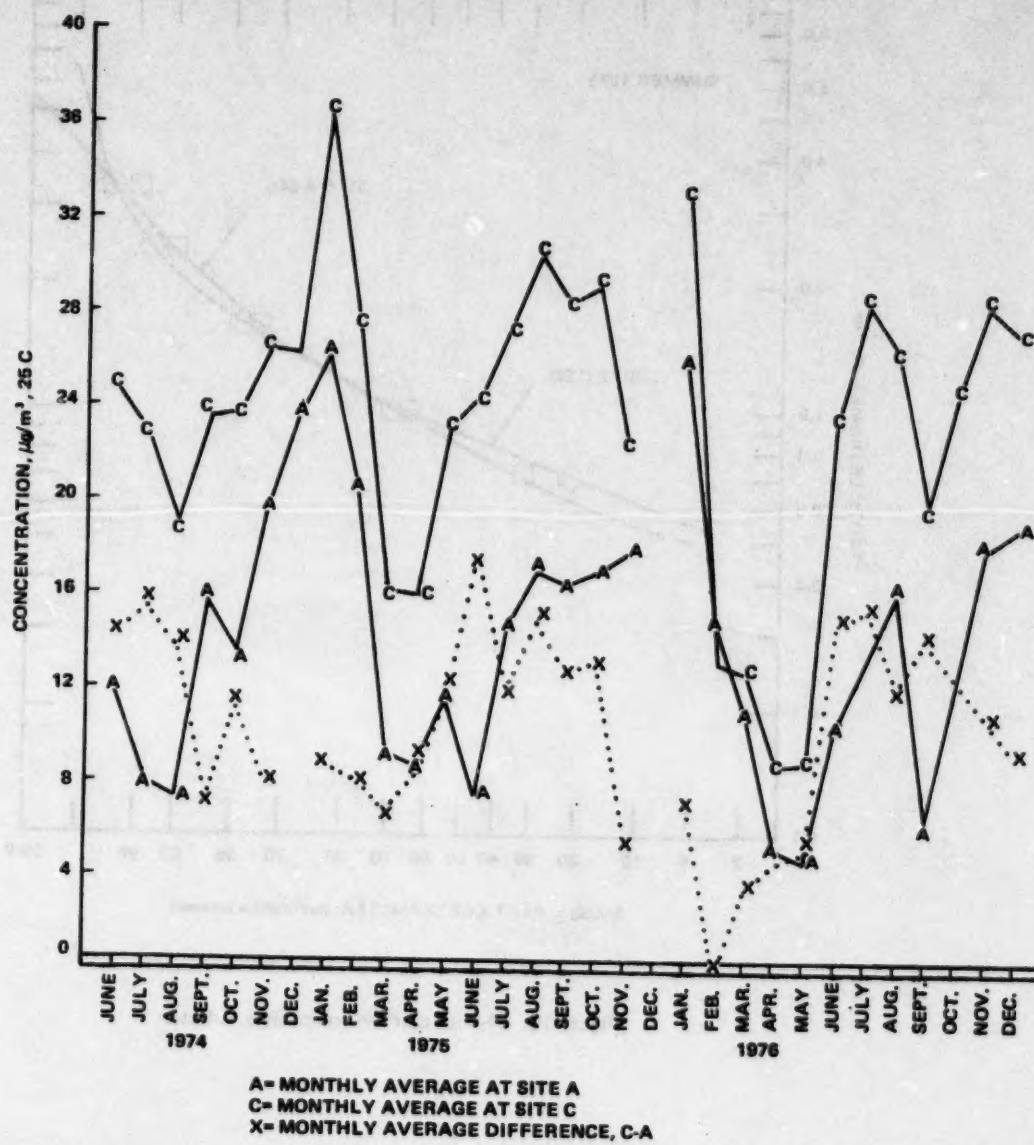


Figure 20. Monthly 24-hour sulfur dioxide levels.

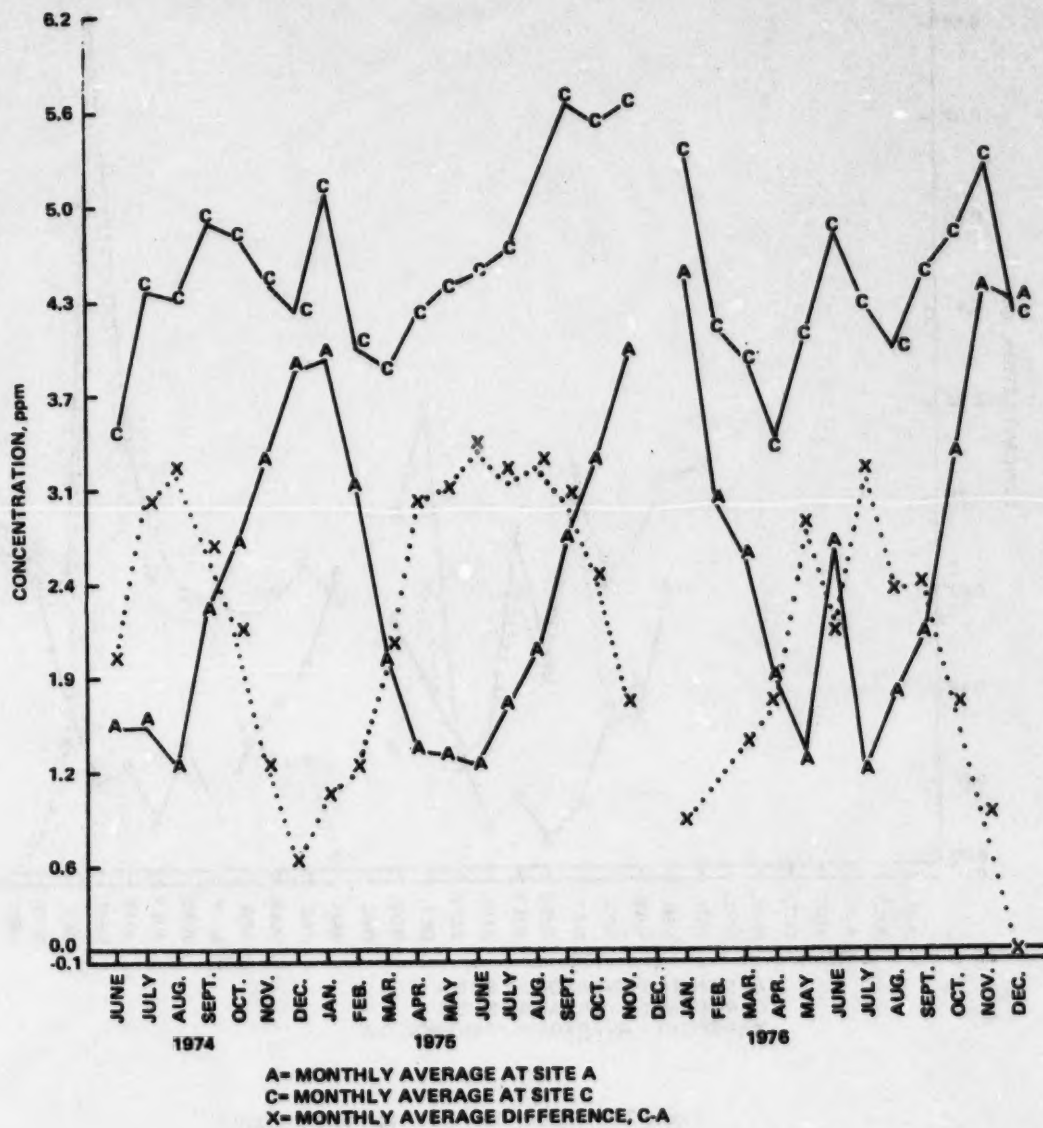


Figure 21. Monthly hourly averages of carbon monoxide.

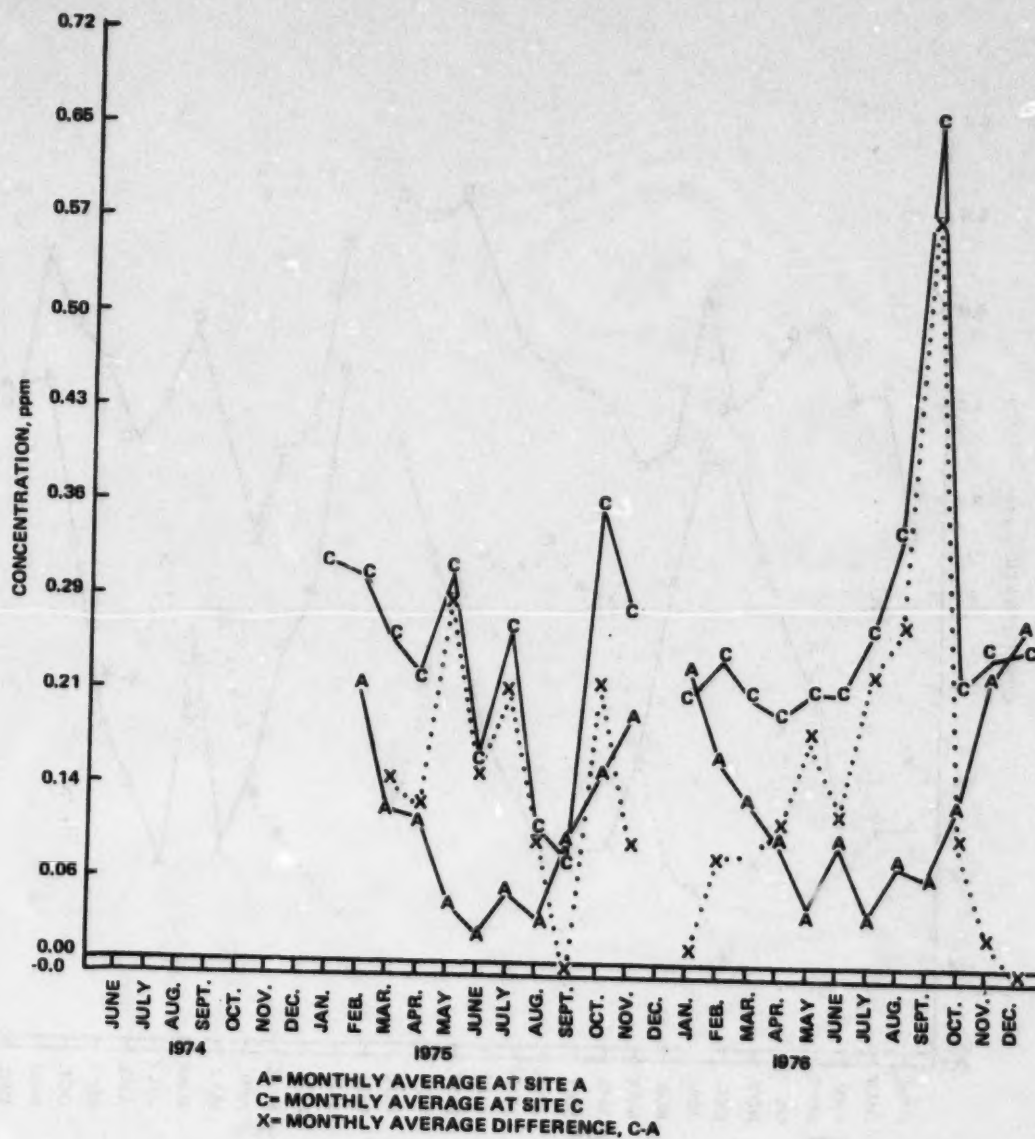


Figure 22. Monthly hourly averages of nitric oxide.

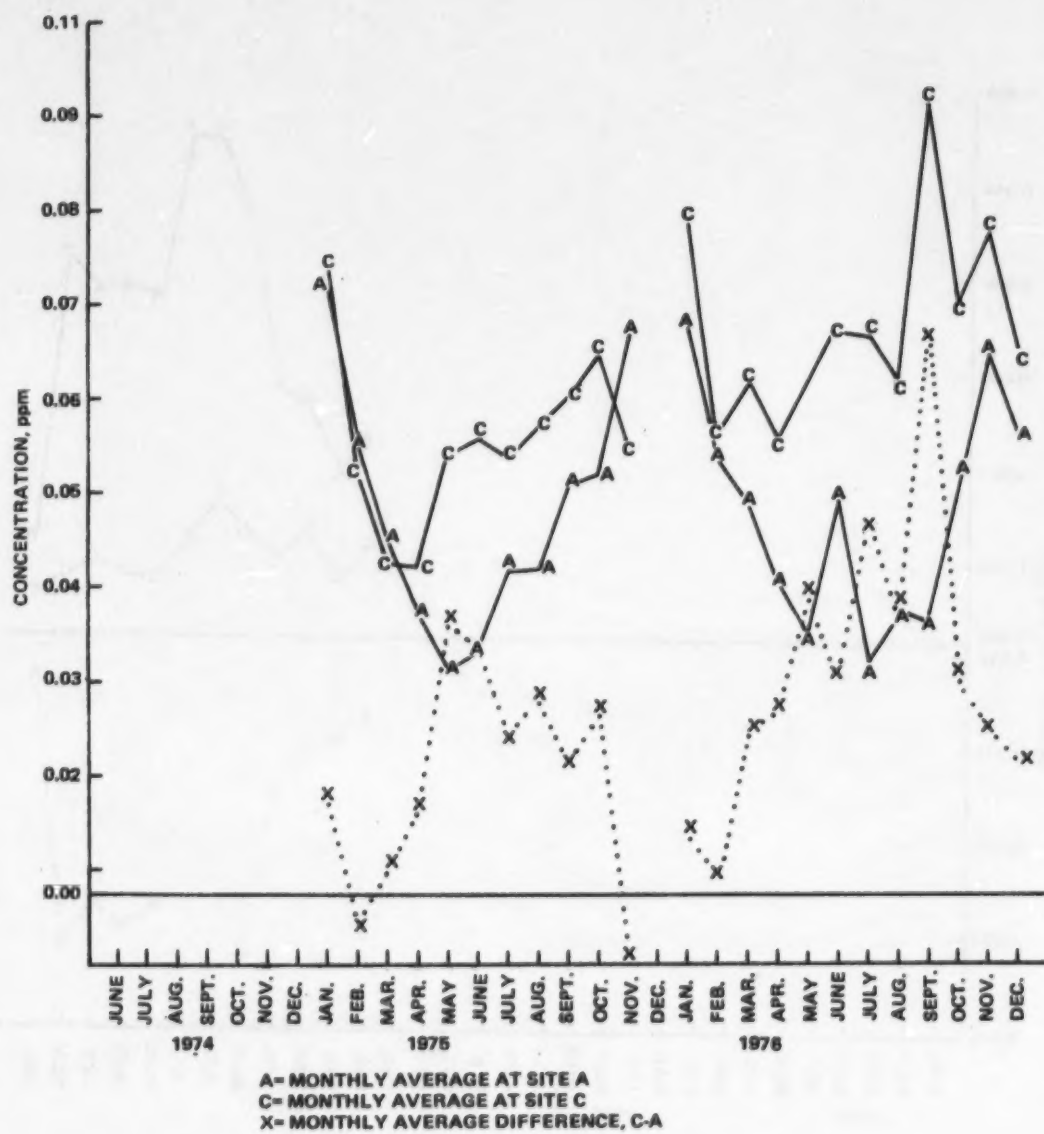


Figure 23. Monthly hourly averages of nitrogen dioxide.

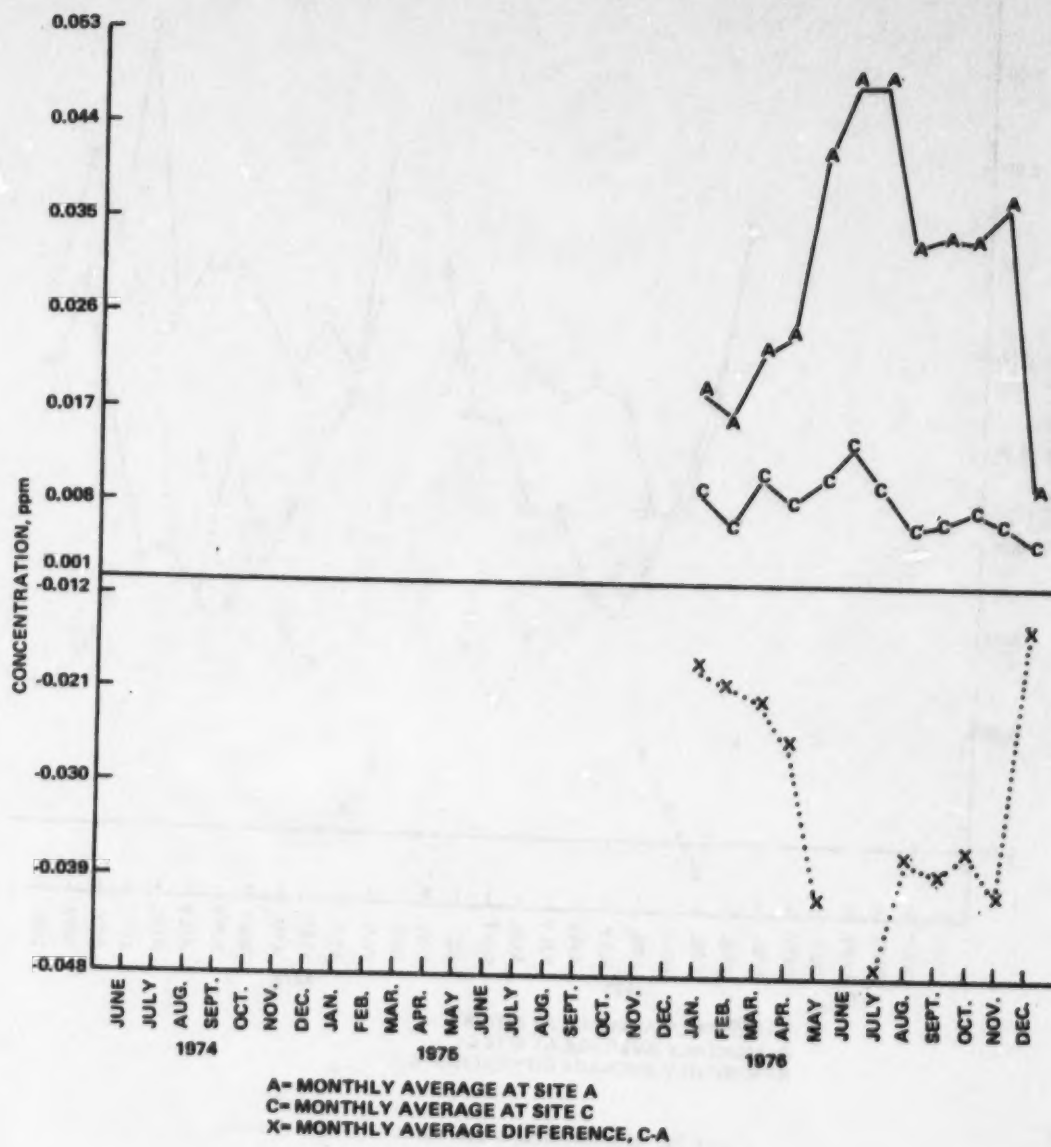


Figure 24. Monthly hourly averages of ozone.

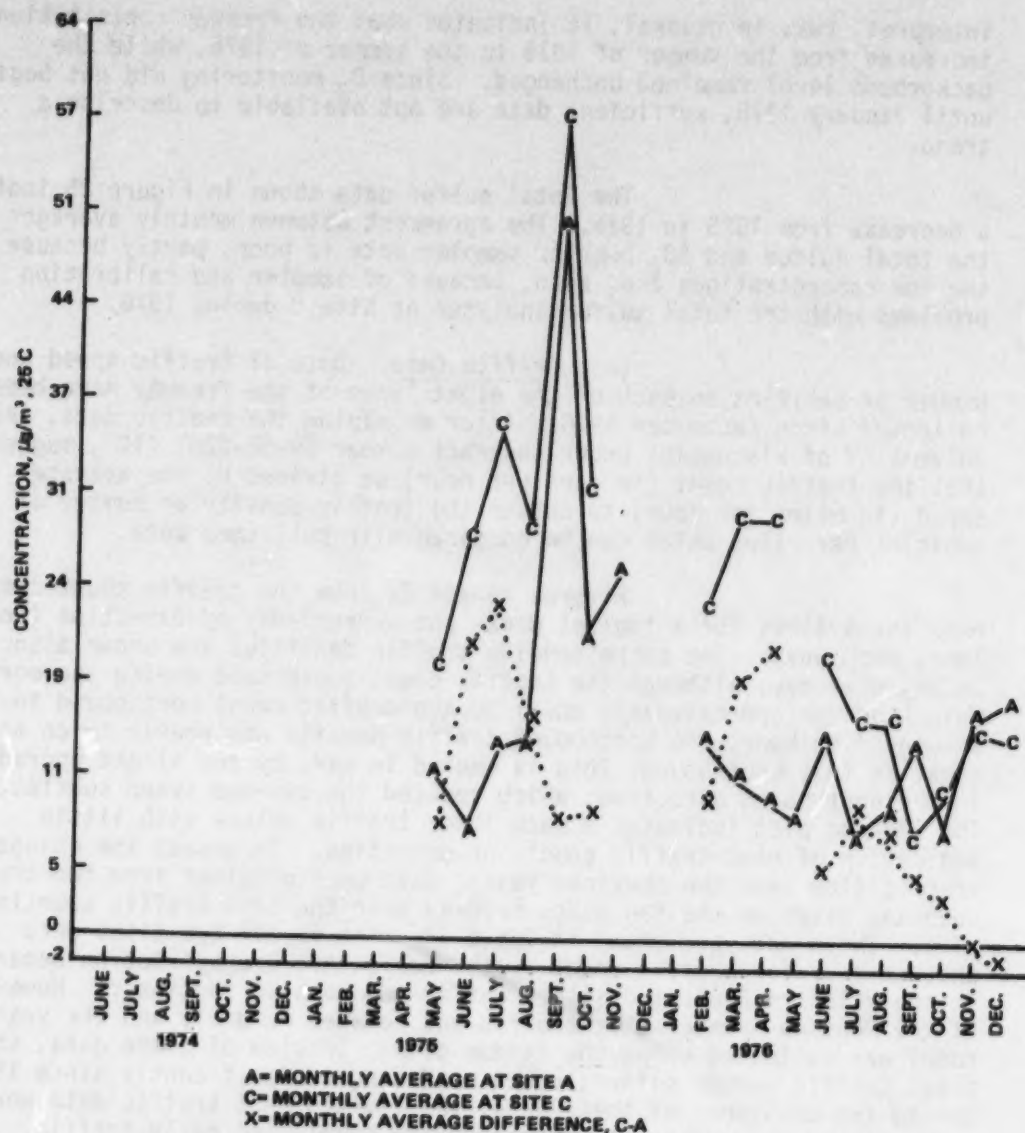


Figure 25. Monthly hourly averages of total sulfur.

interpret, but, in general, it indicates that the freeway contribution increased from the summer of 1975 to the summer of 1976, while the background level remained unchanged. Since O_3 monitoring did not begin until January 1976, sufficient data are not available to describe a trend.

The total sulfur data shown in Figure 25 indicate a decrease from 1975 to 1976. The agreement between monthly averages of the total sulfur and SO_2 bubbler sampler data is poor, partly because of the low concentrations and, also, because of sampler and calibration problems with the total sulfur analyzer at Site C during 1976.

(b) Traffic Data. Data of traffic speed and number of vehicles on each of the eight lanes of the freeway have been collected since September 1976. After examining the traffic data, the University of Wisconsin, under Contract Number 68-02-2261 (12), suggested that the traffic count (in cars per hour) be divided by the average speed (in miles per hour) to obtain the traffic density or number of vehicles per mile, which can be compared with published data.

Figures 26 and 27 show the traffic count composited over the 4 lanes for a typical week- and weekend-day by direction (four lanes each way). The corresponding traffic densities are shown also. On any week day, although the traffic count southbound during the morning rush hour was approximately equal to the traffic count northbound in the evening rush hour, the northbound traffic density was nearly twice as great as that southbound. This is caused in part by the slight upgrade in the northbound direction, which reduced the average speed substantially. The weekend plot indicates a much lower traffic volume with little indication of peak traffic counts or densities. To assess the change in traffic flow over the previous years, data were obtained from two traffic counting sites on the San Diego Freeway near the LACS traffic counting site. These data are shown in Table IV. The former two sites were checked only for traffic count by the California Transportation Department. At the Wilshire Boulevard site, traffic was counted routinely. However, at the Montana Avenue site, traffic was counted randomly and the yearly total was estimated using the random data. In view of these data, the total traffic volume evidently has not changed significantly since 1972. Due to the constancy of these data, the limited LACS traffic data were extrapolated and assumed to represent the hourly and daily traffic patterns since the beginning of the study.

In Los Angeles County, the percentage of registered automobiles equipped with catalytic converters has been compiled quarterly by Rockwell under Contract Numbers 68-02-1766 and 68-02-2292. According to these data (Figure 28), 15 percent of the automobiles registered by the end of 1976 were equipped with catalytic converters. A recent draft report prepared by TRW (13) for the California Air Resources Board proposes

TABLE IV

San Diego Freeway Traffic Flow - Daily Average Traffic Count^a

Counter Location ^{b,c}	Year				
	1972	1973	1974	1975	1976
Wilshire Blvd.	191,000	192,000	189,000	195,000	189,000
Montana Ave.	172,000	173,000	171,000	170,000	177,000

^aData collected by the California Department of Transportation

^bLACS site is located approximately half-way between Wilshire Blvd. and Montana Ave. on San Diego Freeway

^cWilshire Blvd. traffic numbers are actual counts made at a count station just south of the interchange. Montana Ave. numbers are estimates.

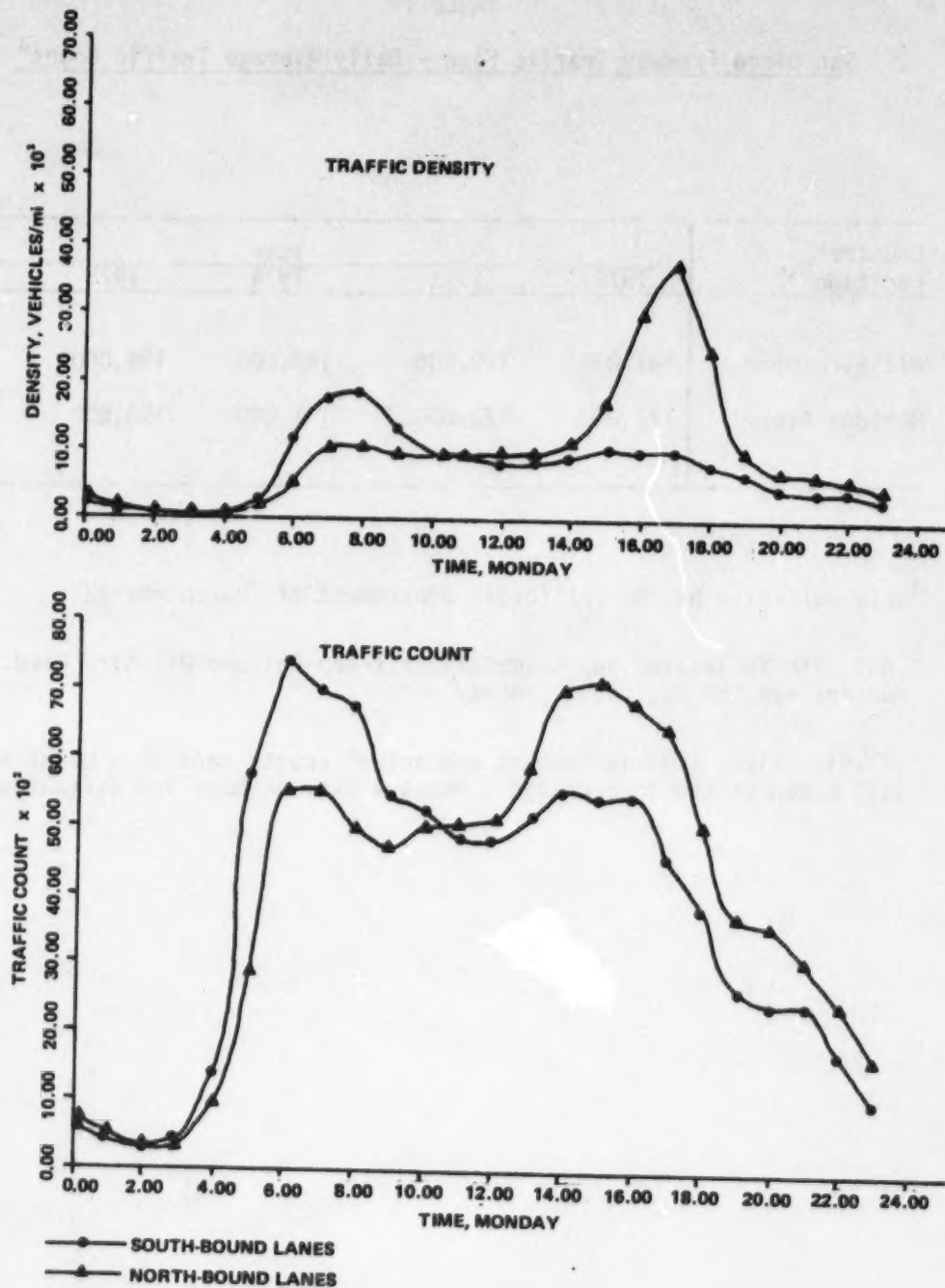


Figure 26. LACS traffic data: daily composite for a Monday.

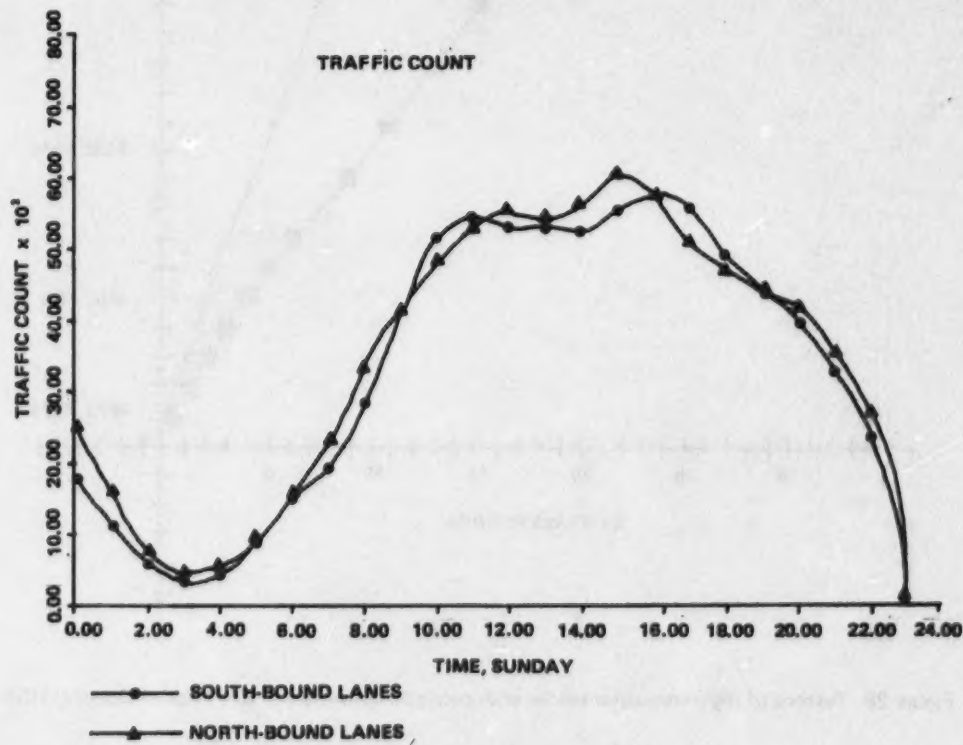
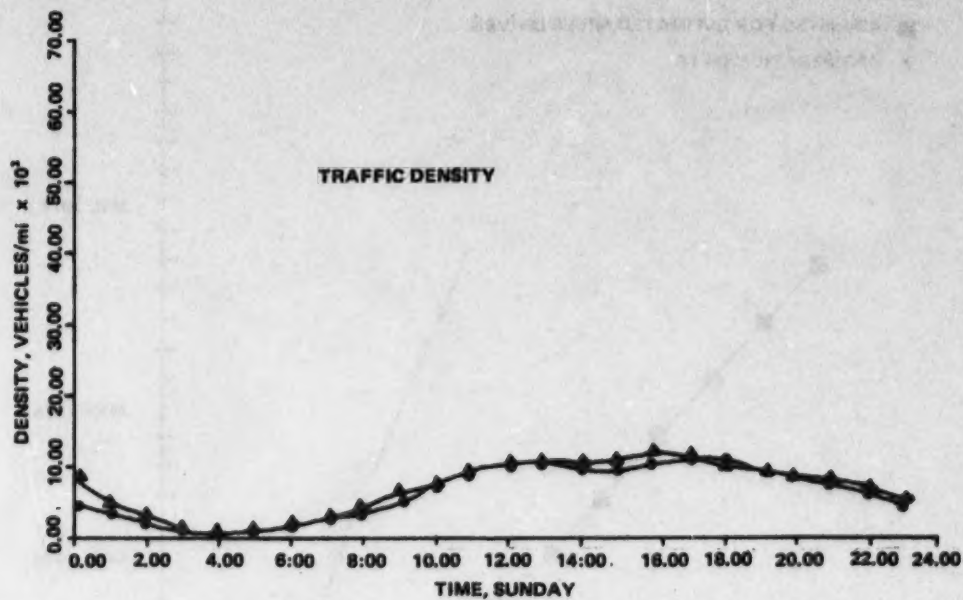


Figure 27. LACS traffic data: daily composite for a Sunday.

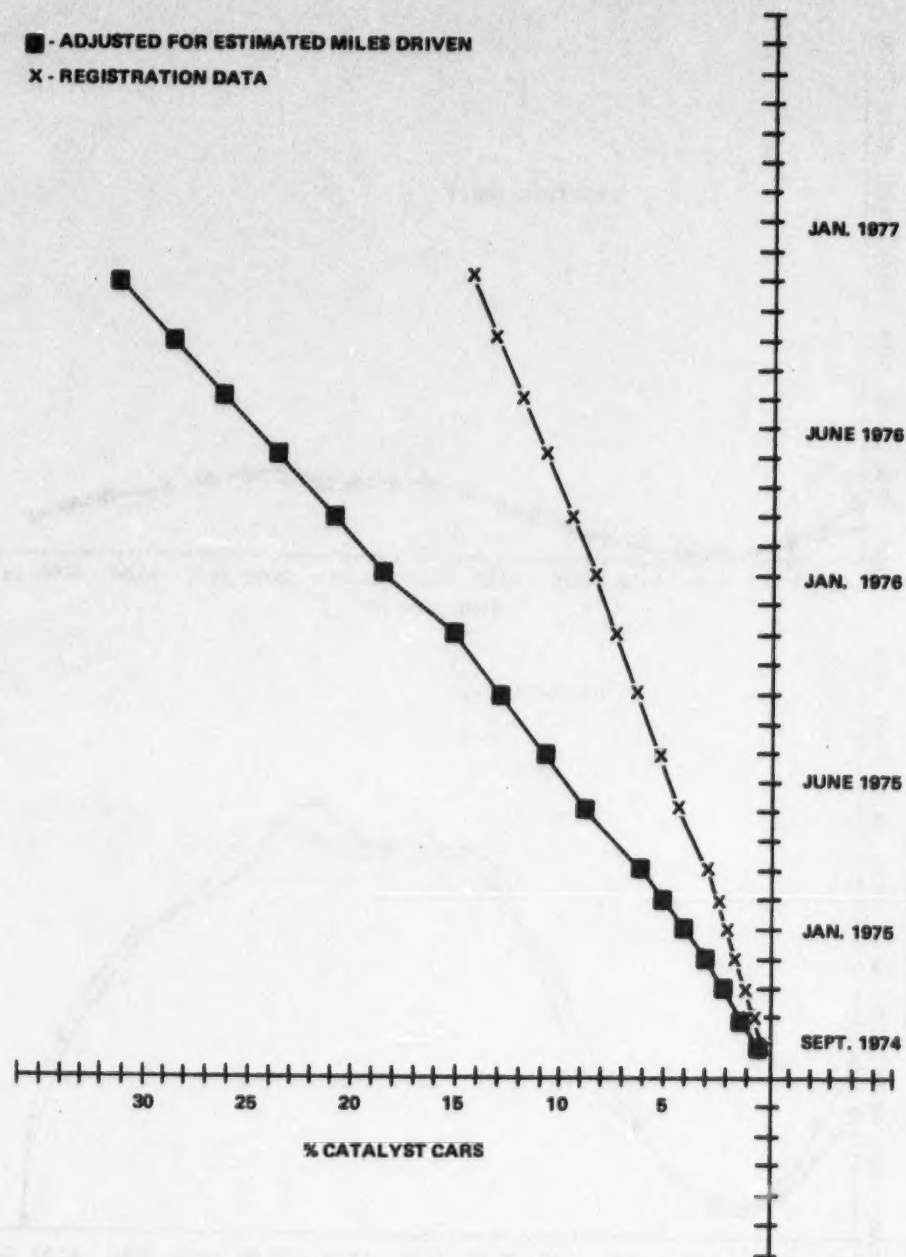


Figure 28. Percent of registered automobiles with catalytic converters in Los Angeles County, 1976.

that the proportion of miles driven by new automobiles is substantially greater than their total number would indicate. For instance, in 1975, a new (1976 model) automobile was estimated to have been driven 2.05 times further than an older automobile. A revised plot based on the Rockwell and TRW estimates, also shown in Figure 28, indicates that at the end of 1976 nearly one-third of the vehicle miles traveled were with catalytic converters. The validity of the TRW estimate will be investigated further.

(5) Ancillary Data

(a) Dustfall Data. The collection of dustfall data began in late 1975 and has resulted in information on the larger particles ($>100\text{ }\mu\text{m}$) found at the four sites. The mass and the Pb, in general, follow the spatial patterns of the high volume sampler monthly averages. However, the Pb data show higher values at Site C as compared with those at Site B than does the data for mass. Presumably, traffic-generated particles larger than $100\text{ }\mu\text{m}$ in size would not travel substantial distances, and prevailing wind direction together would account for the observed trends of mass. The SO_4 , NO_2 , and NH_4 data show larger values at Site A compared with the other sites. This is probably attributable to the dustiness of the open field, which was plowed routinely for weed control near Site A.

(b) Percentage of Collected Data. The percentages of valid data by sampler type are presented in Table V. These percentages have not changed substantially since the beginning of the study.

d. Discussion

The validated LACS data set is voluminous and contains types of data which permit a number of complex data analyses, some of which may continue for several years. In terms of trend analyses on a year-to-year basis, however, only 3 years of data or three data points for each of two seasons are available. Hence, trend predictions are presently somewhat uncertain, although there appears to be significant changes occurring in some of the pollutant levels. The University of Wisconsin, under Contract Number 68-02-2261, is examining the LACS data to identify and quantify data trends.

Of the three monitored pollutants that should be directly affected by the catalyst -- CO, Pb, and SO_4 -- all show some indication of a change in freeway contribution. The levels of CO and Pb decreased approximately 25 percent since 1974, with most of the decreases occurring between 1975 and 1976. These decreases are consistent with the estimated increase in the number of automobiles equipped with catalytic converters and the estimated corresponding increase in unleaded fuel consumption. The three integrated sampling methods that used high volume, membrane, and dichotomous samplers have shown that the SO_4 background level decreased on a 24-hour basis. The 24-hour background measurements decreased about $1\text{ }\mu\text{g}/\text{m}^3$ each year since 1974,³ but the corresponding 4-hour measurements decreased about $1.5\text{ }\mu\text{g}/\text{m}^3$ during the same period.

TABLE V

Percent Data

Method Interval	Wind Speed Hourly	Wind Direction Hourly	Hi-Vol 4-Hour	Hi-Vol 24-Hour	Membrane 4-Hour	Membrane 24-Hour	SO ₂ Bubbler 24-Hour	CO Hourly	NO Hourly	NO ₂ Hourly	S Hourly	Ozone Hourly
June 1974	99.4	100.0	96.7	97.5		80.0	56.7	73.5				
July	33.3	58.1	89.5	92.7		90.0	98.4	82.7				
August	86.8	93.3	100.0	96.3		10.0	90.3	88.6				
September	98.5	98.3	91.7	92.5		20.0	91.7	97.8				
October	90.7	99.9	96.0	100.0		60.0	98.4	86.6				
November	93.8	96.2	100.0	84.4		87.5	100.0	86.7				
December	88.7	73.1	100.0	77.1		83.3	61.1	73.7				
Jan. 1975	100.0	100.0	94.2	100.0		100.0	100.0	100.0	18.2	77.7		
February	97.9	99.9	76.2	89.2		100.0	100.0	79.5	37.6	77.0		
March	94.5	93.0	92.5	97.6		100.0	96.8	62.2	96.8	98.1		
April	98.1	97.6	92.2	91.2		100.0	100.0	96.0	85.8	88.8		
May	99.3	99.5	94.6	95.1		95.0	90.3	90.3	82.2	81.6	89.0	
June	90.4	97.1	97.2	92.5		100.0	98.3	94.7	90.3	90.6	83.7	
July	100.0	97.3	98.9	100.0		100.0	87.1	98.1	95.9	95.3	84.7	
August	99.7	99.7	94.6	90.2		100.0	98.4	97.6	57.9	89.0	85.8	
September	88.7	93.8	92.8	90.0		100.0	93.3	93.1	96.5	95.3	92.5	
October	69.8	70.8	96.2	100.0		100.0	98.4	61.0	69.4	69.4	51.2	
November	83.5	86.9	100.0	100.0		100.0	100.0	96.1	100.0	100.0	26.0	
December												
Jan. 1976												
February	67.2	65.5	35.5	32.9			37.1	61.5	58.9	60.1		41.0
March	98.7	100.0	97.1	90.8		56.6	86.2	87.1	91.7	92.2	77.6	94.0
April	98.1	97.9	83.9	100.0		100.0	95.2	95.0	97.0	97.4	45.4	96.0
May	98.1	98.3	61.8	90.0		100.0	98.3	95.8	95.1	94.9	84.8	96.0
June	100.0	99.9	62.8	91.5		100.0	100.0	95.6	94.3	93.8	47.5	97.2
July	83.9	83.9	63.4	97.5		95.0	90.0	61.7	71.7	71.5	57.8	35.0
August	93.5	92.6	64.0	91.5		100.0	93.5	72.2	31.5	31.4	31.9	30.0
September	82.3	81.1	62.8	97.6		100.0	96.7	96.0	96.6	97.2	96.4	90.0
October	96.8	92.7	62.4	95.1		100.0	96.7	95.2	100.0	93.1	83.1	93.0
November	96.7	97.6	64.4	91.2		90.0	86.9	99.9	98.3	98.7	96.8	97.0
December	2.4	43.3	32.8	47.6		35.0	50.0	45.8	51.3	100.0	96.7	98.0
Overall	87.3	90.3	80.2	90.4		88.7	89.3	82.9	79.6	84.4	71.8	76.0

NOTE: Percent Data = # Actual Valid Readings/# Possible Readings x 100

Since the summer of 1975, the 4-hour membrane and 24-hour high volume sampler data for SO_4 show a small ($<1.0 \mu\text{g}/\text{m}^3$) contribution from the freeway traffic.⁴ The 4-hour high volume sampler data show a consistent 3 to $5 \mu\text{g}/\text{m}^3$ freeway contribution over the same period, except for the last six months of 1976 when the freeway contribution decreased inexplicably to zero. The dichotomous sampler data obtained by the MTB method does not exhibit any change across the freeway. Excluding the 4-hour high volume sampler measurements, the data obtained by other methods indicate that sulfate was generated by the freeway traffic.³ This freeway contribution is estimated to be between zero and $0.5 \mu\text{g}/\text{m}^3$ on a 24-hour basis and 0.5 and $0.7 \mu\text{g}/\text{m}^3$ on a 4-hour basis.

The elevated values on the 4-hour high volume sampler filters suggest artificial SO_4 formation of the glass fiber media. Extensive filter pretreatment was performed on all LACS filters to minimize undesirable reactions. This, in conjunction with the low levels ($<26 \mu\text{g}/\text{m}^3$) of SO_2 present at the LACS site is believed to provide the best data obtainable with glass fiber filters. The 4-hour SO_4 background levels obtained with the high volume samplers, however, are 45 percent greater than those determined with the membrane samplers, but the 24-hour SO_4 high volume sampler averages are only 21 percent greater than the comparable 24-hour membrane sampler averages. Although the membrane and high volume sampler data do not correlate well on a mass basis, a comparison of data for Pb pollutant, which is composed mostly of small particles similar to those of SO_4 , shows fairly good correlation between the methods. This would indicate that the two sampler types are reasonably equivalent in terms of aerosol sampling capabilities for small particles. Further details are available elsewhere (11,14,15).

C. Quality Assurance Activities

EMSL serves as an external auditor of monitoring activities performed within the Catalyst Research Program. Within EMSL, the LACS monitoring program is continuously audited through blind samples and sample splits. During the year, intermittent audits were conducted of CO , SO_2 , THC , NO_x , and ozone used in the animal exposure chambers used by HERL/Cincinnati. Similar audits were performed of SO_2 , ozone, and CO at HERL/RTP as used in their human exposure chambers. The purpose of these audits is to verify exposure levels.

A split sample analysis quality assurance program was initiated in July of 1974 when collection of air samples began in LACS. Aliquots of the air samples are analyzed by the contractor, Rockwell Air Monitoring Center (RAMC), and EMSL. The split sample program was begun to determine the comparability between analyses performed by RAMC and EMSL and to determine analytical variability on real air samples.

In November 1974, a blind audit quality assurance program was initiated for RAMC by EMSL. The blind audit program was initiated to investigate and document the precision and accuracy achieved by RAMC during the analysis of ambient air samples collected in LACS.

Both the blind audit and split sample program have changed since their beginnings in 1974 to accommodate fluctuations in the number of samples collected in LACS, variability of the analytical results, and EMSL's growing experience in conducting external audit programs. Table VI gives the pollutants, types of audit sample and frequencies of both the blind audit and split sample programs currently followed.

Sulfate and nitrate are spiked on the same filter for the blind audit samples; lead is spiked on a separate filter. RAMC then extracts and analyzes these samples as they would a regular sample. Sulfur dioxide blind samples are special freeze-dried tetrachloromercurate-sulfite solutions. RAMC thoroughly rinses the audit sample from a sealed vial with absorbing reagent before analyzing as a normal 50 ml bubbler sample.

The main use of the blind audit results is to document chronologically the precision and accuracy achieved by RAMC. A second major use of the blind audit data is to determine if any portions of the analytical methods employed by RAMC need improvement. The third use of the blind audit results is to point out a large bias or variability that might occur across all levels for a pollutant during an analytical period. If this situation occurs, both the EPA project officer and RAMC are immediately notified. This situation has never occurred during the blind audit program.

Since the blind audit samples are not real air samples, but synthetic samples, the split sample program serves to show variabilities encountered on analysis of real samples. Secondly, the split sample results serve as a measure of the reproducibility on real samples between two laboratories which are using the same analytical methods. Initially, the split sample program was conducted at a much higher analysis rate than is shown in Table VI but the larger time delay between analyses, the information obtained in the blind audit results, and the continuing comparability between EMSL and RAMC, allowed EMSL to cut back to the current split sample rate.

Summary reports for both blind and split sample analysis are periodically made to the EPA project officer and to RAMC (16,17). Split sample results are reported at the end of each quarter, while blind audit results are reported at twenty-five week intervals.

TABLE VI

Blind Audit and Split Sample Frequencies

<u>Pollutant</u>	<u>Sample Type</u>	<u>Audit Frequency</u>	
		<u>Blind Audit</u>	<u>Split Sample</u>
Sulfate	Hi-Vol Filter	10/week	6/month
Nitrate	Hi-Vol Filter	10/week	6/month
Lead	Hi-Vol Filter	7/week	6/month
Sulfur Dioxide	Bubbler	10/bi-weekly	None

The external quality assurance program consisting of split and blind sample analyses has been useful in improving, verifying, and quantifying the quality of data obtained in LACS. Both the lead and sulfate analytical procedures have been improved because of the results obtained in the external audit program. Detection and correction of analytical problems has been timely enough to avoid invalidating large blocks of analytical data. Besides upgrading analytical methods, a chronological history of accuracy and precision is available from the start of this project. Figures 29 through 32 show the agreement of RAMC with the spike result for sulfate, nitrate, lead, and SO_2 , respectively. With the exception of lead, RAMC agreed with the spike value $\pm 5\%$. In the case of lead, however, agreement for 1976 was only 87% of the spiked values. For the split sample results, sulfate and nitrate were within $\pm 5\%$ and lead $\pm 10\%$ (18).

IV. PROBLEM AREAS

A. Fuel Collection and Analysis

1. Fuel samples are collected by the Regional Offices. We have experienced problems in obtaining fuel samples from Region IX, and have not received samples since the summer of 1976. We will remedy this situation in 1977 by hiring a contractor to obtain the samples.

2. There has been a reoccurring problem when attempting to relate the analytical results of the fuels samples to the amount of fuel consumed in the area of concern -- in particular, Southern California. This link is vital to the emission modeling program, reviewing trends of pollutant concentration affected by the catalyst and interpreting impact of control technology.

B. Monitoring -- LACS

Without a specific sulfuric acid monitor, inferences about sulfuric acid emissions are based on indirect measurements, e.g., sulfate. This problem will be solved when the state-of-the-art H_2SO_4 analyzers become available. Similarly, an ammonia monitor is needed, since no satisfactory instrumentation is available.

C. Quality Assurance

Problems identified through the auditing program have been found and corrected.

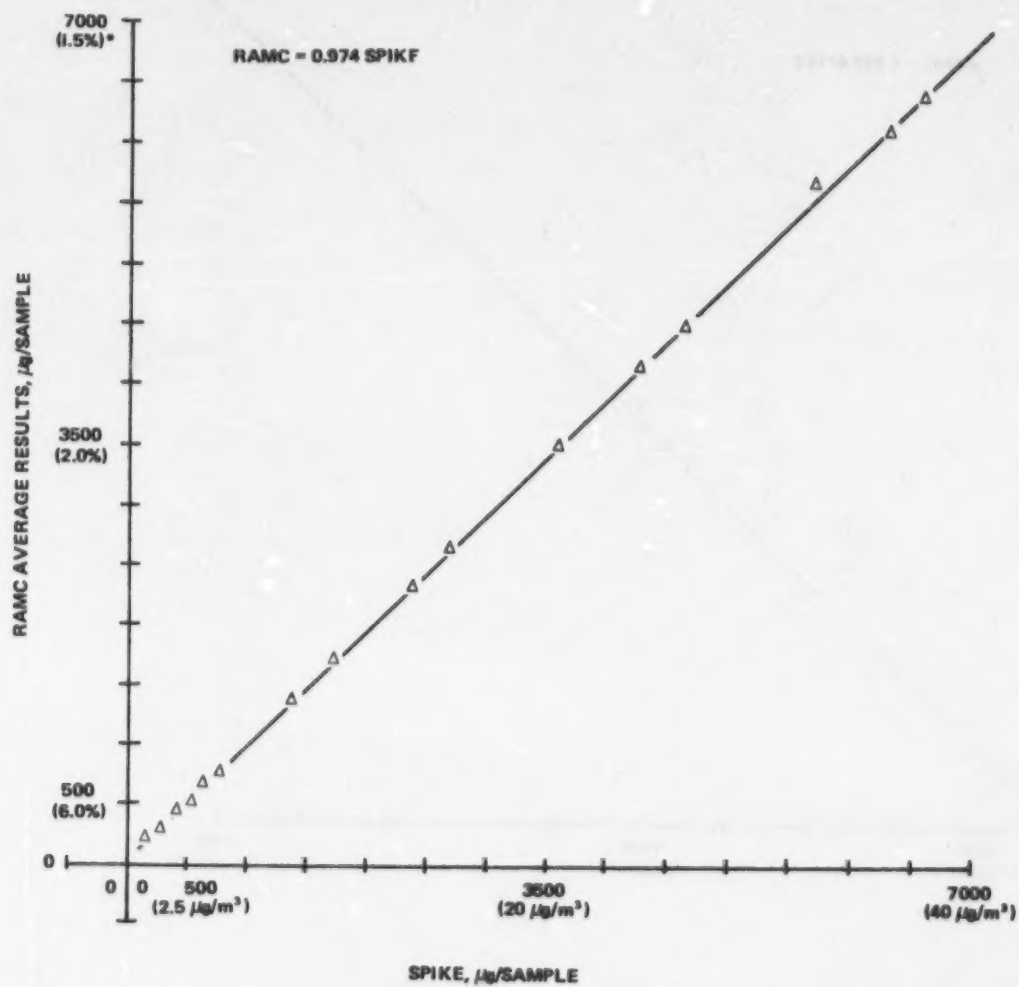


Figure 29. Comparison of RAMC blind sulfate results with spike values.

*RESULTS EXPRESSED AS COEFFICIENT OF VARIATION IN PERCENT OF AVERAGE RESULT

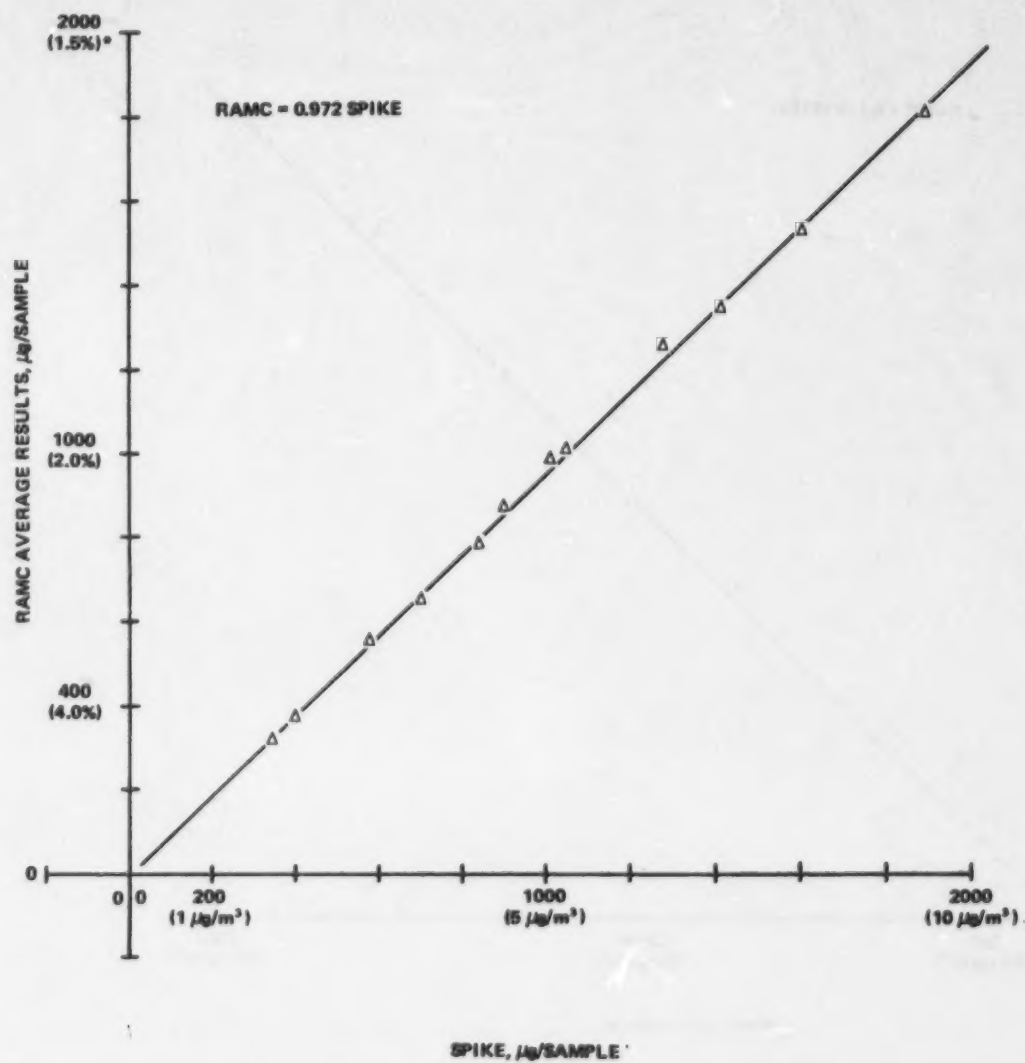


Figure 30. Comparison of RAMC blind nitrate results with spike values.

*RESULTS EXPRESSED AS COEFFICIENT OF VARIATION IN PERCENT OF AVERAGE RESULT

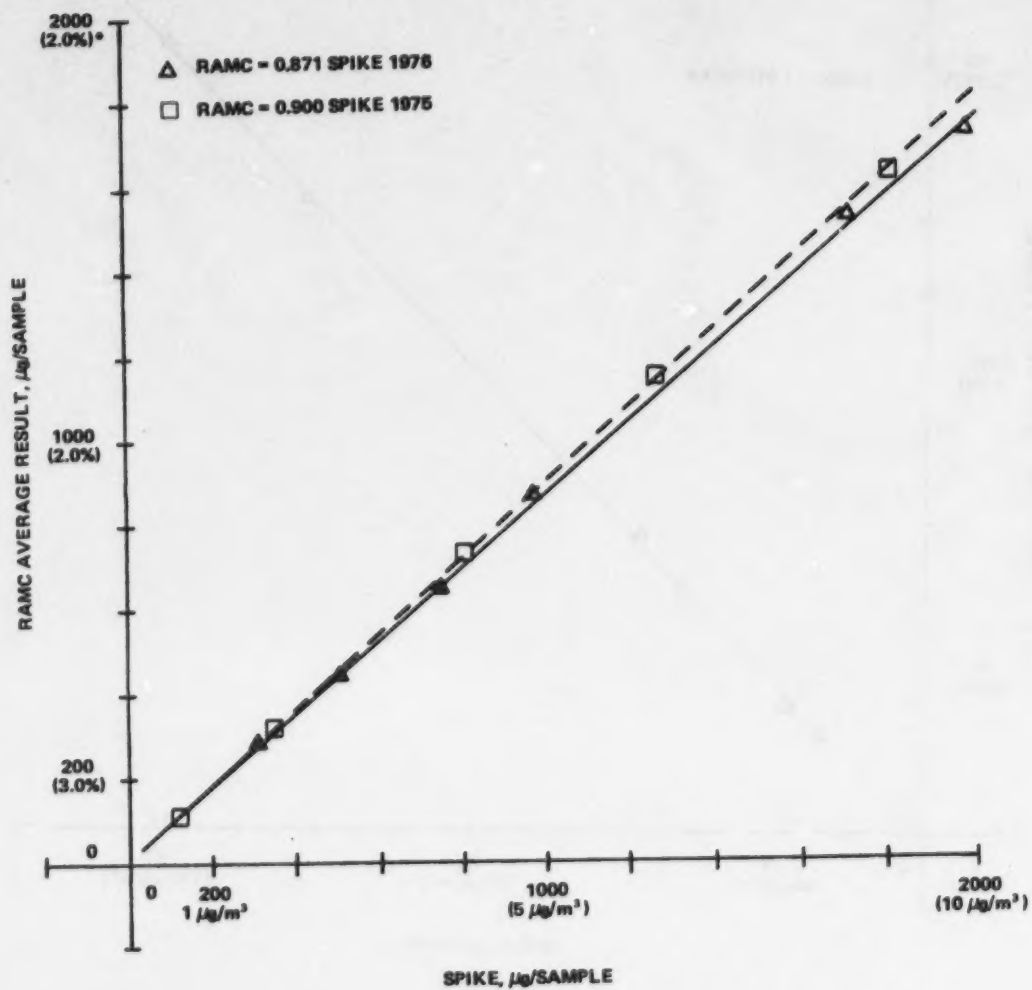


Figure 3I. Comparison of RAMC blind lead results with spike values.

*RESULTS EXPRESSED AS COEFFICIENT OF VARIATION IN PERCENT OF AVERAGE RESULT

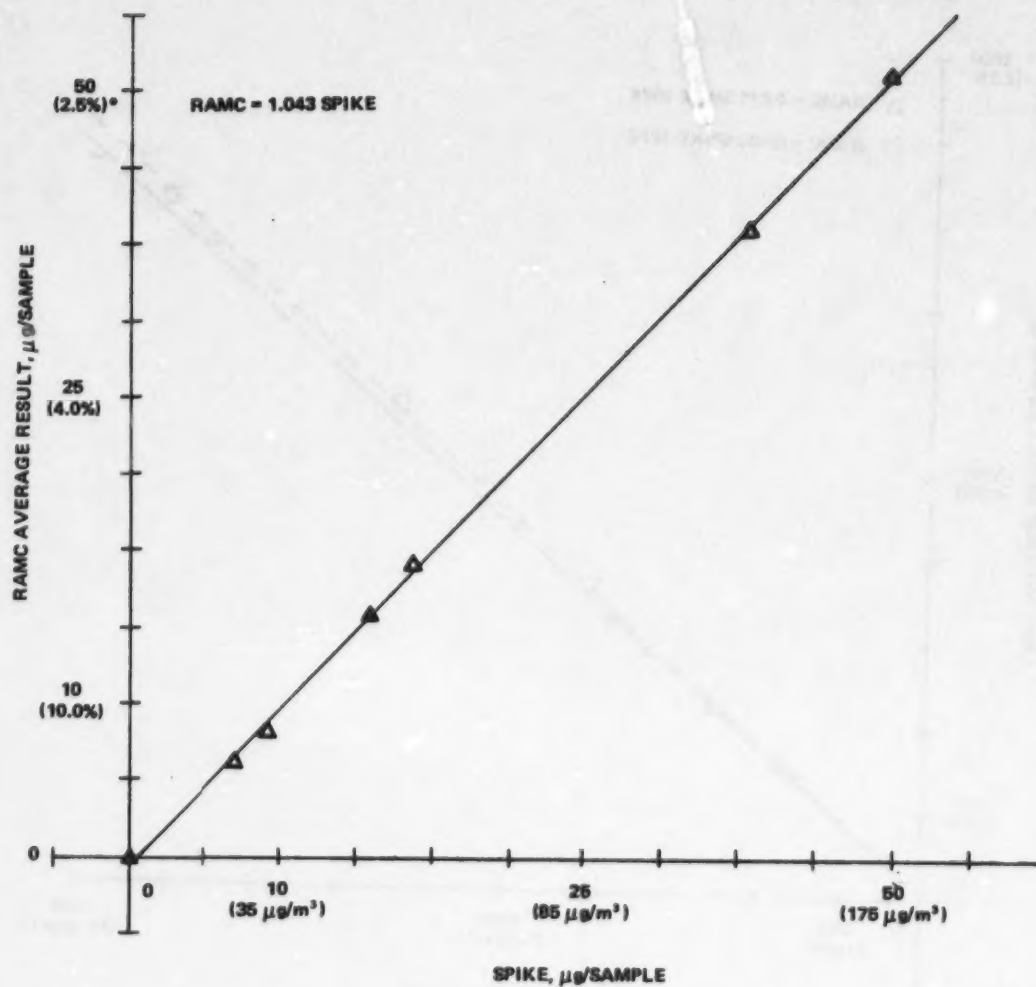


Figure 32. Comparison of RAMC blind sulfur dioxide results with spike values.

*RESULTS EXPRESSED AS COEFFICIENT OF VARIATION IN PERCENT OF AVERAGE RESULT

V. PLANS FOR FUTURE RESEARCH

A. Fuel Collection and Analysis

Since manganese (Mn) is being used by refiners to replace lead as an anti-knock compound, effects to the emission control device as well as analytical screening techniques to detect presence of Mn in the gasoline need further study. Progress has already started within EMSL to measure Mn by atomic absorption spectroscopy (AAS) and steps to standardize the procedure are being considered by the American Society of Testing and Materials (ASTM).

Other method development and fuel data include polycyclic organic matter, such as BaP and benzene.

B. Monitoring -- LACS

The following items concern the future research program for LACS:

1. There is a need to continue to evaluate the impact of catalysts on air quality. This will be increasingly important as new catalyst-type vehicles and additional diesel traffic are added to the traffic mix. Our present data base and site are extremely well suited for assessing effects of transportation control strategies on air quality data. Only through a long-term monitoring study under appropriate quality control can theoretical and laboratory findings be verified from which regulatory decisions should be based. At least two more summer seasons of data are necessary to establish a reliable trend using present sampling technology.

2. The addition of a sensitive, reliable continuous sulfuric acid analyzer will be made when available to verify our off-roadway estimates of ambient H_2SO_4 levels. Assuming an acceptable H_2SO_4 analyzer will be available in the near future, two year's of summer data should be gathered to demonstrate the relationship between sulfate measurements and sulfuric acid aerosol.

3. There is a need for additional in-roadway measurements taken at the fixed site collected in the median as well as mobile sampling around the LACS area. Knowledge of spatial variability together with our temporal variability studies will provide us the means from which theoretical population exposure estimates can be verified. In addition, in-vehicular concentrations should be determined as needed.

4. There is a definite need to quantify the amount of sulfate artifact formation on filters used to monitor sulfate at the LACS site, especially for 4-hour measurements.

5. It is intended that time series models will be developed to concurrently employ data from all sites to estimate spatial and temporal variability across the freeway. This will include fixed in-roadway and mobile monitoring data.

6. The present data base contains information in examining a variety of other equally important issues associated with transportation control; e.g. (a) establishment of the proposed Pb standard; (b) input to the formulation of an oxidant control strategy; (c) examination of the cross-freeway relationships of the oxides of nitrogen and ozone; and (d) verification of the relationships between auto emission measurements and actual ambient levels at the roadside. It should be noted that an additional two summer seasons of data will greatly augment this data base.

7. At present, EPA is concerned with environmental insult due to toxic substances, some of which are emitted from mobile sources, such as polynuclear aromatics, benzene, and BaP. Maintaining surveillance of air quality in proximity of major roadways could serve to identify and determine trends of air quality due to pollutants from mobile sources for the purpose of determining the need for and effect of control measures.

C. Quality Assurance

Ongoing research will be continued. Auditing of animal studies conducted at HERL/RTP will begin in 1977.

IV. CONCLUSIONS

A. Fuel Collection and Analysis

The following observations are made based on fuels analysis research supported by the catalyst program.

1. The content of sulfur in unleaded gasoline in Southern California is approximately twice that found in New York samples and the content of sulfur in the 3 grades of gasoline is consistently higher in Los Angeles than San Francisco.

2. Sulfur content in Los Angeles appears to be decreasing within grades, but the range of measured levels is narrowing.

3. Percent aromatic content is increasing, with no lead gasoline grade higher than other grades.

4. Method development and standardization for analysis of gasoline for a number of constituents including sulfur, phosphorus and lead has been realized.

B. Monitoring -- LACS

The following observations are made following the analysis of the body of information collected from the monitoring effort at LACS.

1. Based on the across freeway difference, the use of the catalyst and unleaded fuel have resulted in substantial decreases (25%) in CO, Pb, and TSP while the background levels remained essentially consistent.
2. The freeway contributions of $\text{SO}_4^{=}$ have increased less than 10% while the background levels decreased.
3. Oxides of nitrogen over background levels have increased 50% from $38 \mu\text{g}/\text{m}^3$ to $56 \mu\text{g}/\text{m}^3$ from 1975 to 1976.
4. Lead is significantly higher on the weekends (~60%) despite a reduction of traffic volume (~20%).
5. The 4-hour evening peak traffic period from 1500 to 1900 hours is a favorable period in which to detect cross-freeway differences.
6. The sulfate loading on 4-hour high volume samples is strongly influenced by artifact $\text{SO}_4^{=}$ formation.
7. Traffic patterns are markedly different between weekdays and weekends. Friday has the highest volume of traffic (~210,000 vehicles/day compared to ~190,000 vehicles/day during other weekdays).
8. Traffic density (count/speed) is a better descriptor of emissions for continuous pollutant empirical modelling purposes.
9. At the end of 1976, the estimated percentage of catalyst-equipped cars may be as high as 30%.

C. Quality Assurance

Through a carefully controlled quality assurance program consisting of external audits and split samples, an extensive body of ambient roadside data of known quality has been generated.

APPENDIX A-1

PRECISION OF LACS SAMPLING AND ANALYTICAL METHODS

Two special studies have been conducted at the Los Angeles Catalyst Study sites in an effort to identify and quantify the major sources of error inherent in the sampling and analytical methods employed.*

First, co-located high volume samplers were operated concurrently for twelve 24-hour periods at a location 700 feet upwind from the freeway. Following equilibration and weighing, each exposed filter was analyzed in duplicate (using center and end strips) for concentrations of lead, ammonium ion, nitrate ion and sulfate ion by each of two laboratories. The results were used to construct estimates of the amount of variability (i.e., "variance component") between samplers, between laboratories and within laboratory. In addition, effects of strip position (center versus end) and the time lag between sample collection and chemical analysis on reported pollutant concentration were estimated.

The second study consisted of operating five samplers (two high volume samplers with glass fiber filters, two membrane samplers with cellulose ester filters and a single membrane sampler with teflon filters) at each of two sites (upwind and downwind) on a 4-hour interval (3-7 p.m.) for twelve days. In addition to final weight, each filter was analyzed in duplicate for sulfate ion concentration by each of two laboratories. Estimates were obtained for the between sampler, between laboratory and within laboratory components of variance. Finally, the effects of site and method on reported pollutant concentrations were investigated.

The major results drawn for the 24-hour high volume sampler study are as follows:

- (1) Sample collection from co-located instruments is not a significant source of error (<5%).
- (2) Laboratory variability (same filter) is significant except for SO_4 (0%)**: Pb (7.5%), NH_4^+ (38.2%), and NO_3^- (3.8%).
- (3) Variability among filter strips is the largest source of error for the above pollutants: Pb (17.2%), NH_4^+ (11.2%), NO_3^- (6.2%), and SO_4 (3.1%).
- (4) Variability among chemical analyses within a laboratory is relatively minor for all pollutants: Pb (2.4%), NH_4^+ (3.2%), NO_3^- (1.7%), and SO_4 (2.3%).
- (5) Strips cut from the center of filters tend to be slightly (<5%) higher in concentration than those cut from the ends.

*A report is available from the Office of the Director, EMSL/RTP.

**Percentages are based on coefficient of variation.

- (6) The time lag between sample collection and chemical analysis is a serious source of error in the determination of NH_4^+ .
- (7) Total measurement variability is 18.9%, 7.5%, 3.9%, for Pb , NO_3^- , and SO_4^{2-} , respectively.

The major conclusions drawn from the 4-hour high volume and membrane sampler study are as follows:

- (1) The overall TSP precision for 4-hour high volume samples is only slightly greater than that for 24-hour samples (5.6% versus 5.2%).
- (2) Though sample collection and laboratory are significant sources of error for SO_4^{2-} determination from 4-hour high volume samples, the overall SO_4^{2-} precision is only slightly greater than that for 24-hour samples (5.9% versus 3.9%).
- (3) The overall TSP precision for 4-hour membrane samples (cellulose ester filters) is approximately three times that for 4-hour high volume samples (14.9% versus 5.6%).
- (4) The overall SO_4^{2-} precision for 4-hour membrane samples (cellulose ester filters) is approximately three times that for 4-hour high volume samples (17.6% versus 5.9%).
- (5) TSP concentrations appear to be dependent upon filter material employed (i.e., cellulose ester or teflon), though not necessarily upon sampler type (i.e., high volume or membrane).
- (6) SO_4^{2-} concentrations are very dependent upon filter material employed with the following ranking in the order of descending concentration: high volume glass fiber, membrane cellulose ester, membrane teflon.

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APPENDIX B

THIRD ANNUAL CATALYST RESEARCH PROGRAM REPORT

Prepared by

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I. INTRODUCTION

The Environmental Sciences Research Laboratory/North Carolina has primary responsibility within EPA for the conduct of research pertaining to the atmospheric transformation and transport of airborne pollutants. Essential related research responsibilities pertain to (1) the characterization of emissions to the atmosphere, and (2) the development of measurement methodology for such characterization and for determining the nature and distribution of pollution in the ambient environment. Consequently, the Laboratory was prepared to play an important role in the Agency's research effort to assess the potential impact of automotive catalyst-generated "sulfate" when this issue was surfaced and accepted research assignments in the following areas:

1. Develop measurement methodology for the qualitative and quantitative characterization of emissions emanating from catalyst-equipped vehicles and of the air affected by such emissions. (Measurement Methods)
2. Ascertain the nature and magnitude of sulfur-bearing and related emissions under typical vehicle operating and malfunction conditions. (Emission Characterization)
3. Apply measurement methodology to characterize the pattern of human exposure within the localized area. (In-Roadway Study)
4. Establish the relationships between emissions and exposure of the public at risk and develop models for predicting the potential impact of such emissions on the quality of the air to which the population at maximum risk is likely to be exposed. (Modeling)

The attached report documents the research efforts of the Environmental Sciences Research Laboratory during the 1976 calendar year, organized according to the laboratory branch primarily responsible for its conduct. A short commentary on the catalyst program is offered here, as an overview of the subject.

The issue that is being addressed by the catalyst research program belongs to a growing class of problems--a second generation of issues that have their origin in otherwise successful solutions to initially-perceived problems. It underscores the importance of "technological assessment" wherever technology is to be applied to broad-based societal problems. It calls for a new attitude in research and development, one that looks beyond the short-range results to the long-range consequences, with a view to bringing these in balance. The catalyst, which promises to be an effective deterrent to the traditional automotive pollutants, is inherently capable of generating other pollutants of great potential concern.

TABLE 1
SUMMARY OF ESRL CATALYST PROGRAM MEASUREMENT METHODOLOGY

Task Number (FY-77)	Description	Milestones	Funding (\$K) FY76	Funding (\$K) FY77
<u>AMBIENT AIR MEASUREMENT METHODS</u>				
CA-23	Sulfuric Acid Sampler/Analyzer Cabot Corp. Contract 68-02-2402	5/77 Begin Delivery 2/78 Complete Delivery 8/78 Final Report	75	35
CA-31 BE-37	Sulfuric Acid Generator for Ultrafine Particles University of Minnesota Grant 80-4600 Northrop Contract 68-02-2566	9/77 Deliver UM Generator 9/77 Report on Northrop Generator	71	50
CA-24	Development of a Gas Chromatographic System For NH ₃ University of North Carolina-Charlotte Grant 80-4413	7/77 Interim Report 8/78 Final Report	18	0
CA-21	Continuous Monitor for Particulate Sulfur Compounds Oregon Graduate Center Grant 80-4750	10/77 Assemble Instrument	30	35
CA-11	Development of Methodology for Sulfuric Acid Atlantic Research Contract 68-02-2247	6/77 Report on Interferences	64	10
CA-12	Development of a Portable Collection System for Atmospheric Sulfuric Acid Southern Research Inst. Contract 68-02-2234	6/78 Final Report	64	50
CA-32	Rural and Urban Measurements Environmental Measurements, Inc. Contract 68-02-2484	6/77 Final Report	9	20
<u>MOBILE SOURCE MEASUREMENT METHODS</u>				
CA-15	SO ₂ Compliance Test Instrument Aeronutronic-Ford Contract 68-02-2448	10/77 Deliver Prototype	60	14
CA-16	SO _x Compliance Test Instrument Ford Motor Co. Res. Lab. Contract	10/77 Deliver Prototype 2/78 Final Report	110	0

TABLE 2

Summary of Sulfate Emissions Factors by Manufacturer
(Olson Study - 1975 and 1976 Model Year California Cars)

Manufacturer	No. of Vehicles	Test Average		mean SO _x mg/mile		
		No.	Mileage	FTP ¹	1st CFS ²	HFET ³
Fleet	101	1	3395	4.3	17.1	22.3
General Motors	44	1	3752	1.96	9.55	17.55
		2	7428	3.03	8.86	13.25
		3	11274	1.10	3.74	6.39
Ford	26	1	3352	8.36	27.69	26.85
		2	7614	3.40	9.91	14.51
		3	12730	2.64	6.73	7.72
Chrysler	20	1	3039	5.17	24.26	27.86
		2	7617	3.04	15.31	24.70
		3	11537	3.41	8.03	15.96
AMC	5	1	2879	3.26	12.09	9.36
		2	5189	0.58	4.35	9.70
		3	7906	1.43	7.12	3.19
Foreign (Datsun, Toyota, VW)	6	1	2706	2.01	6.84	13.48
		2	5377	1.23	3.56	4.73
		3	11525	1.01	2.51	2.28

Notes:

1. FTP = 1975 Federal Test Procedure - Urban Driving Cycle (19.9 mph)
2. CFS = Crowded Freeway Simulation (35.0 mph)
3. HFET = Highway Fuel Economy Test (49.9 mph)

The technological assessment approach as applied by the Environmental Sciences Research Laboratory recognizes the critical importance of defining the future consequences of general usage of catalysts in automotive pollution control. This is causing a change in emphasis in the Laboratory from retrospective research to more prospective research. Major efforts are underway to ascertain the definitive chemical and physical structure of the atmospheric pollution that is likely to be associated with the automobile of the future, independent of and combined with other traditional pollutant sources. Predictive models are being developed and tested to estimate the related pollutant dosages that the public is likely to be exposed to in various risk situations and, in particular, the situations of maximum risk. The composition of the pollution and the potential dosages will depend to a large degree on the "design" of the catalyst that will find broad future use. Accordingly, it will depend on the changing performance of the catalyst with changing operational requirements imposed on it through various driving patterns and engine modes. It will also depend on the changing performance with age of the catalyst and changing composition of future fuels, lubricants, and additives. It will depend on changing fuel mileage requirements in the future. These emission characteristics of the catalyst are being explored to the extent that the state-of-the-art, resources, and manpower permit. It calls for the development and acquisition of innovative sampling and analytical equipment that will not alter the complex physical dimensions and finite chemical composition of the emissions being analyzed. The report that follows addresses the status of these efforts, presents preliminary findings, and indicates future directions and plans.

II. MEASUREMENT METHODS

A. Ambient Air Measurement Methods

1. Sulfuric Acid Sampler/Analyzer Cabot Corporation/Fowler (PI) Contract 68-02-2402

In 1974 ESRL initiated a program with Cabot Corporation to develop an automated aerosol sampler/sulfuric acid monitor. As a result of the GM/EPA Sulfate Dispersion Experiments in which the Cabot sulfuric acid monitor was successfully employed, Cabot was further funded to fabricate and deliver several coupled automated aerosol sampler/sulfuric acid analyzers to EPA. The acid aerosol is sampled through a NH_3 denuder into a dichotomous sampler so that only the fine aerosol-fraction is collected on a Teflon filter. The filter is then automatically moved into a volatilization zone where sulfuric acid is selectively volatilized from the filter into a flame photometric detector.

The first prototype of the automated aerosol sampler/sulfuric acid analyzer was tested during the October 1976 Los Angeles In-Roadway Measurement Study. During these tests a number of malfunctions occurred and after a view of the design, Cabot was requested to make modifications to improve the reliability of the analyzer and to separate the sampler from the analyzer to simplify operation and maintenance of the two components. These modifications caused a 6-month delay in delivery of the samplers and analyzers.

2. Sulfuric Acid Generator for Ultrafine Particles
University of Minnesota/Liu (PI)
Grant R804600

The GM/EPA Sulfate Dispersion Experiment indicated that ultrafine particles should be used in exposure studies designed to determine the effects of sulfuric acid on animals. A grant was awarded to the University of Minnesota to fabricate a sulfuric acid generator that will deliver particles in the 0.02 to 0.5 μm size range. This generator has been coupled to an animal exposure chamber for use by the Health Effects Research Laboratory. Northrop Services, Inc. is also fabricating a generator for use with animal exposure studies.

3. Continuous Monitor for Particulate Sulfur Compounds
Oregon Graduate Center/Huntzicker (PI)
Grant R804759

A program was initiated to develop a flame photometric detector for continuous, in situ measurement of total particulate sulfur and certain individual sulfur compounds. The technique is based on coupling a diffusion SO_2 denuder to a flame photometric detector. The denuder removes the gaseous sulfur compounds and only permits the particulate sulfur to enter the photometric detector. Modulated heating of the aerosol upstream of the denuder permits differentiation between sulfuric acid and ammonium sulfate. To optimize the operation of the heater-denuder, the flash volatilization of several sulfate compounds was studied. Several different types of denuders are being fabricated to permit the removal of SO_2 , H_2S , CH_3SH , and CH_3SSCH_3 . A prototype system, suitable for use in field studies, will be assembled and evaluated.

4. Development of a Gas Chromatographic System for NH_3
University of North Carolina at Charlotte/Cooke (PI)
Grant R804413

The University of North Carolina-Charlotte was awarded a grant to (a) develop a gas chromatographic system which will permit the analysis of sub-part-per-billion concentrations of NH_3 , and (b) develop improved chemical converters for chemiluminescent NO_x and NH_3 monitors. For the gas chromatographic system, a column was developed which permits passage of low ppb NH_3 concentrations with near ideal peak symmetry. The gas

chromatographic system will be coupled to a chemiluminescent detector, being developed by ESRL, and used in field studies to measure ambient concentrations of NH_3 in rural and urban locations across the United States.

5. Development of Methodology for Sulfuric Acid
Atlantic Research/Valentine (PI)
Contract 68-02-2247

The objective of this task was to develop methodology to selectively measure sulfuric acid in the range of 0.25 to 50 $\mu\text{g}/\text{m}^3$. The project was directed toward identifying reagents which would react with sulfuric acid aerosol forming adducts which could be selectively analyzed in the presence of sulfate. The current status and achievements to date are as follows:

- Three candidate reagents for the formation of adducts were identified.
- The formation of adducts by the reagents was demonstrated.
- The adducts were isolated and their likely composition was determined.
- SO_2 is released by decomposing the adducts at 200°C.

Major problem areas exist with regard to the specificity of the reaction adduct and the decomposition efficiency of the adducts.

6. Development of a Portable Collection System for
Atmospheric Sulfuric Acid
Southern Research Institute/Barrett (PI)
Contract 68-02-2234

As a first step in development of a collection system for sulfuric acid, an evaluation of the interferences that may occur when samples containing sulfuric acid are collected on a filter was conducted.

Results indicate that the collected sulfuric acid aerosol is subject to interference by alkaline gases and by other particulate materials in the sample air. Strong interference is caused by gaseous ammonia, particulate calcium carbonate, and ambient particulate matter from an urban oxide and a silicate clay soil; and relatively little or no interference is caused by nitrogen dioxide, sulfur dioxide, fly ash, soot, and the vapors of pyridine and phenol. These conclusions suggest that research on the formation of sulfuric acid-adducts which could be selectively analyzed should be continued and expanded.

7. Rural and Urban Measurements
Environmental Measurements, Inc.
Contract 68-02-2484

Prototype instrumentation for SO_2 , NH_3 , NO_x , and H_2S was evaluated using a mobile van equipped with a mapping and data acquisition system. The

field evaluation was accomplished in a cross-country run from Denver, Colorado, to Raleigh, North Carolina, in August 1976. Measurements were made of rural and urban concentrations along the route. Data from this study demonstrated the operation characteristics of an NH_3 denuder and capability of a new prototype Meloy SA-285 flame photometric detector to measure sub-part-per-billion concentrations of SO_2 and H_2S .

B. Mobile Source Measurement Methods

Several successful analytical techniques for SO_2 and SO_4 mobile source emissions have been reported in previous annual reports. While in-house efforts to standardize these analytical techniques are continuing, no further in-house developments are planned under the catalyst program.

Contract programs for routine SO_2 and H_2SO_4 mobile source monitors are currently active at Aeronutronics-Ford² and at Ford Motor Company Scientific Research Laboratory. However, there is no experimental performance data available for either the UV-correlation spectrometer for SO_2 or the microcoulometric sulfate monitor at this time.

III. EMISSIONS CHARACTERIZATION

Since Catalyst Research Program-supported efforts in previous years have adequately defined H_2SO_4 emissions factors for low-mileage vehicles in the 1975 and 1976 vehicle years, as well as for many prototype automobiles aimed at future HC, CO, and NO_x emissions standards, the current year's programs concentrate on two issues which have not yet been adequately studied. The first program involves a study of sulfuric acid emissions factors for 101 in-use California cars performed by Olson Laboratories, Inc. While initial emissions factors for this fleet were reported in the 1976 Catalyst Research Program report, currently available data from this recently-completed project shows a rapid decrease in H_2SO_4 with increasing mileage. The second program (in-house) aimed at characterization of both gaseous and particulate pollutants for a group of 24 California-standard cars. The majority of these cars were European imports, utilizing at least a measure of catalytic NO_x reduction; all were tested under both certification tune and under simulated rich malfunction. Significant levels of HCN and NH_3 were found with both dual-bed and three-way catalyst configurations. Additional major findings from both studies are given below.

A summary of the Olson data is given in Table 2. While the initial fleet average SO_4 emission rate of 17.1 mg/mile was surprisingly low, the observed decrease to 10 mg/mile at 7,000 miles and to 5 mg/mile at 11,000 miles is remarkable. This decrease is about evenly distributed throughout the major manufacturer subsets of this fleet. Thus, it appears that catalysts lose their sulfate-forming activity more rapidly than their ordinary capacity for HC and CO.

Other major conclusions include:

1. HC and CO remain low and mostly within Federal standards in the first year of life for California cars.
2. NO_x emissions rates are mostly greater than applicable California standards for 1975 and 1976 model years.
3. Average California fuel sulfur levels are about the same as the national average.

Goals of the in-house characterization study of California cars included determination of H₂SO₄ and other particle emissions under a variety of driving cycles and determination of H₂S, COS, NH₃, and N₂O emissions under both standard and malfunction conditions. HCN and ammonia emissions were traced to rhodium-containing catalysts specifically. Previous experience with such catalysts indicated rather low activity for sulfuric acid formation. Subsequently, all 4,000 mile emissions data cars in the 1977 certification program were tested over urban, expressway, and highway driving cycles. HCN, NH₃, and SO₄ data for the highest HCN cars are given in Table 3. HCN yields from catalyst-equipped cars are usually at least one order of magnitude below those for non-catalyst automobiles. When three-way or dual-bed systems fail rich of stoichiometry, HCN emission rates increase dramatically as a product of the catalytic reduction of NO. However, the maximum value found so far has been about 0.15 grams/mile; rich malfunction also accelerates CO emissions in the order of 20-70 grams/mile. Therefore, CO will always be 200-500 times greater in concentration than HCN. Since OHEE has indicated the health effects of HCN are similar, apparently the CO formed poses a greater health threat than HCN. Ammonia toxicity at present is less well-defined. HCN and NH₃ monitoring will be continued for future catalyst designs, but no significant problem is anticipated.

Future in-house work will concentrate on measurement of trace components such as low molecular weight amines, cyanogen, and nitromethane from catalyst cars. Sulfuric acid emissions monitoring for 1978 model year Federal-standard cars will also be continued as an adjunct to specific characterization programs designed for this group.

IV. IN-ROADWAY STUDY

Studies carried out during the previous year, particularly the General Motors/Environmental Protection Agency test roadway sulfate dispersion experiment, indicated that off-roadway levels of sulfate emitted from catalyst-equipped cars would be near background and not constitute an air pollution hazard. Attention was then turned to the roadway itself, since this was the only place where sulfate levels from catalyst-equipped cars might become high enough to be hazardous. In this event, occupants of vehicles in the roadway could be affected.

TABLE 3

HCN Formation

1977 California-Standard Certification Cars

Vehicle	Control System	Driving Cycle	Pollutant emission rate, gr/mile							
			Malfunction mode				Standard tune			
			HCN	CO	NH ₃	NO _x	HCN	CO	SO ₂	NO _x
Volvo, auto. trans. 3-way		urban	0.046	22.4	0.518	0.56	0.001	2.7	10 ⁻⁴	0.33
Volvo, manual tr. 3-way		urban	0.033	18.3	0.400	0.42	0.001	2.7	10 ⁻⁴	0.52
Saab auto. trans. 3-way		expressway	0.078	22.0	0.705	0.87	0.003	1.0	10 ⁻⁴	0.53
Mercedes 280	dual bed	urban	0.045	65.7	0.251	0.60	10 ⁻⁴	1.7	0.008	1.33
AUDI 100LS	ox. cat.	urban	0.006	9.9	0.028	1.15	0.003	1.9	0.001	1.24
1976 Chrysler	lean burn	urban	-	-	-	--	0.011	4.5	0.001	2.56

Sulfate levels in the roadway would, of course, vary considerably depending upon the mix of vehicle emission factors, traffic density, and meteorological conditions. Also, the exposure would depend on the length of time the vehicle occupants would be in the roadway. Horowitz and Papetti of EPA developed statistical curves showing the probability of exposure to various levels of sulfate by vehicle occupants (see Appendix B-1). These curves were developed using a substantial data base of vehicle usage during the 6 to 9 a.m. period on weekdays and the best available information on predicted roadway levels of sulfate. This statistical analysis served to define the type of in-roadway sampling program that would be needed to obtain an estimate of the exposure hazard of vehicle occupants.

To implement this study, a contract was awarded to Rockwell International Air Monitoring Center to participate in and support a field program that would involve aerosol scientists from the University of Minnesota, Washington University at St. Louis, and the California Institute of Technology. The study was conducted in Los Angeles during the last two weeks of October in 1976 and was designed to demonstrate the feasibility of making in-roadway measurements with instruments installed in moving vehicles. If feasibility could be demonstrated a larger scale in-roadway measurement program could be conducted in the following year.

A. California Institute of Technology (Caltech) Measurements

The group from the California Institute of Technology which participated in this study was associated with Professor S.K. Friedlander and was primarily organized and led by Dr. Susanne Hering. Caltech served as host for this study and provided invaluable laboratory space and services. Caltech also operated a van which made measurements at the background site selected for each day. The instruments that were in the van are listed in Table 4 along with the name of the organization responsible for analyzing the filter aerosol samples collected.

The low pressure impactor (LPI) used by Caltech is a single-jet, eight-stage impactor with 50% collection efficiency at cut sizes of 0.02, 0.05, 0.11, 0.25, 0.5, 1.0, 2.0, and 4.0 μm aerodynamic diameter. The 0.25 and 0.11 μm cutoff stages were calibrated with polystyrene latex spheres and the 0.05 and 0.02 μm cutoffs are based on theoretical calculations. Comparisons with the electrical aerosol analyzer (EAA) for laboratory-generated ammonium sulfate and sulfuric acid aerosols is reasonably consistent with the theoretical calculations. The impaction surfaces above 0.5 μm are coated with Vaseline to minimize particle bounce-off to the lower stages. The lower stages were analyzed for sulfur content by flash volatilization in a flame photometric detector.

B. University of Minnesota Measurements

The University of Minnesota participants in this study were associated with Professor K.T. Whitby, and a key role in the field operations

TABLE 4

Instruments in the Caltech Van

Manual Dichotomous Sampler (Caltech-AMC)

Low Pressure Impactor (Caltech)

Two Mass Sampler (Washington University)

Ammonia Sampler (AMC)

Meteorological Measurements

and data analysis was entrusted to Bruce Cantrell. The main activity of the University of Minnesota was to operate a mobile laboratory in freeway traffic and at background sites. For most experiments, air samples were collected through tubes which had inlets just above the headlights of the van. Table 5 gives a listing of the equipment in the van. Because the aerosol-measuring equipment requires several minutes to determine a particle size spectrum, bag samples were collected about every four minutes, and the size distribution of the aerosol in the bag was determined. Data from the trace gas measuring instruments were recorded every half second, and then averaged over the time of each bag fill. The aerosol and gas data resulting from one bag fill was computed and printed in tabular form for each run on board the van.

A trichotomous sampler designed and built at the University of Minnesota was used in this field study for the first time. Its purpose was to collect size fractionated aerosol samples on Teflon filters and to include in the fractionation, a cut between the nuclei and accumulation mode size range. A dichotomous sampler splits the aerosol into a flow containing the large particles collected on filter A, and the particles smaller than $3.5 \mu\text{m}$ collected on filter B. A portion of the flow to filter B is drawn to an EAA, where it is further classified. The nuclei mode particles are drawn in the drift tube toward the central collector rod, and are collected on filter D. The larger particles remain the outer portion of the flow and are collected on filter C. These filters were designed to fit into the Cabot sulfuric acid analyzer (SAM).

An automated dichotomous sampler was also operated in the University of Minnesota van and samples collected were analyzed for sulfuric acid concentration with SAM or for hydrogen ion H^+ , and sulfate (SO_4) concentrations by AMC.

An observer aboard the University of Minnesota van made sample counts of catalyst-equipped cars on October 26, 27, and 28 and estimated the number of catalyst cars to be approximately 28% of the total.

C. Washington University Measurements

The Washington University participants in the October field program were associated with Professor E.S. Macias. Their main activity was to operate an instrumented automobile on the freeways and at the background sites. The Washington University car and the University of Minnesota van operated as a team and generally followed the same sampling schedules and itineraries.

The instrumentation in the automobile included a Two-Mass sampler, an LBL dichotomous sampler, and an aerosol charger which included the capability of adding ammonia to the sampler air flow and passing the sample through a temperature-programmed heat tube. The LBL sampler used an air intake outside the car from October 19 to 23 and sampled from inside the car with the windows open from October 24 to 30. The Two-Mass sampler and the charger always sampled outside air.

TABLE 5

Nomenclature and Description of Instruments in
the University of Minnesota VanMeteorology

WDIR, WD	Wind direction, clockwise degrees from north
WSPD, WSP	Wind speed, kilometers/hour
TOUT	Outside temperature, °C
TIN	Inside temperature, °C
TEAA	EAA classifier temperature, °C
DEWPT, TDP	Dew point, °C
RH, RELHUM	Relative humidity, percent

Gas Measurements

SO ₂	Sulfur analyzer, Monitor Labs, Model 8450
O ₃	Ozone monitor, Dasibi Corp., Model 1003-AH
CO	Carbon monoxide monitor, Energetics, Sci. Inc.
NO, NO _x	Chemiluminescent NO-NO _x -NO ₂ analyzer, Thermo-Electron Corp., Model x ₁₄

Aerosol Measurements

EAA	Electrical aerosol analyzer; Thermo-Systems, Model 3030
CNC	Condensation nuclei counter; Environment One, Model RICH 1000
Royco 220, R220	Optical particle size counter, Royco Model 220
LBL	Automated dichotomous sampler, Lawrence Berkeley Labs.
TCS	Trichotomous sampler, University of Minnesota
LPI	Low pressure impactor, Kech Lab., Caltech

The Two-Mass sampler separates particles into two size fractions. Coarse particles are impacted on a glass fiber filter; the remaining particles are collected on an identical high-efficiency glass fiber filter. Samples were collected on a portion (0.3 cm^2) of a light-weight (1.2 mg/cm^2) low pressure-drop glass fiber filter (Ballflex 70) with a consistent and low sulfur blank of 0.3 to $0.5 \text{ } \mu\text{g/cm}^2$. The fine particle cutoff is designed to have a 50% collection efficiency at $3.5 \text{ } \mu\text{m}$.

Analysis of the water-soluble particulate matter collected in 2-hr intervals with the Two-Mass sampler was performed using a flash vaporization/flame photometric system. The analyzing system consisted of a flash vaporization vessel, flame photometric detector, integrator and a capacitor discharge across a tungsten boat, resulting in resistance heating to 100°C . A water extract of each sample is prepared by punching out a circular filter segment (0.6 cm^2) containing the aerosol deposit. An aliquot of the extract is evaporated on the tungsten strip and then vaporized into the FPD.

The roadway sulfur values as measured with the Two-Mass and FPD systems are calculated by taking the difference between the data obtained with two different samplers in two different vehicles. The mean of all these differences is $-0.04 \text{ } \mu\text{g/m}^3$ sulfur, and the standard deviation of the differences about the mean is $0.55 \text{ } \mu\text{g/m}^3$ sulfur.

Table 6 is a comparison of the in-roadway sulfur with sulfur measurements taken at the background sampling site.

D. EPA - Rockwell International Measurements

A portion of the filter samples collected in the October field program were returned to Thomas Dzubay, EPA, Research Triangle Park, N.C., for analysis by X-ray fluorescence (XRF). The data obtained for lead on filters from the trichotomous sampler in the University of Minnesota van shows clearly that large amounts of lead ($> 10 \text{ } \mu\text{g/m}^3$ in some cases) are present on the freeway in the nuclei mode size range. These data also provide a confirmation of the proper operation of the trichotomous sampler.

The main role of the Rockwell International Air Monitoring Center (AMC) in the field program was to provide analytical chemistry services for the rapid turn-around analysis of filter samples. Over 400 wet chemical determinations were performed on 76 filters and 71 filters were analyzed at Caltech by the Cabot SAM.

Aerosol samples were collected on $1 \text{ } \mu\text{m}$ fluoropore filters by various sampling devices in the three vehicles described previously and then were returned to the laboratory at Caltech. There the filters were placed in desiccators lined with glass filters coated with oxalic acid. The humidity in the desiccators was generally near ambient.

TABLE 6

Average Daily Net Roadway Sulfur from Two-Mass
Sampler in the Washington University Car

<u>Date - October</u>	<u>Aerosol Sulfur Concentration, $\mu\text{g}/\text{m}^3$</u>		
	<u>Average Freeway</u>	<u>Average Background</u>	<u>Difference F-B</u>
19	6.3	9.04	-2.75
20	4.68	4.88	-0.21
21	3.04	2.27	0.77
22	3.14	2.59	0.55
24	2.96	2.92	0.04
25	2.64	2.75	-0.11
26	0.34	0.11	0.23
27 a.m.	0.58	0.28	0.30
27 p.m.	0.55	0.29	0.26
28	0.46	0.57	-0.11
		Measure	-0.11
		Standard Error	0.98

The filters were returned daily to the AMC where they were ultrasonically extracted and titrated for strong acid by the Gran procedure. The ammonium ion concentration was determined by an ion selective electrode, and sulfate, bromide and nitrate determined with an ion chromatograph.

Table 7 summarizes the sulfate results using the LBL dichotomous samplers. It can be seen that as a general rule there is no significant difference in the total small particle sulfate numbers on and off the freeway. This was true even on October 26 when the Santa Ana winds were blowing and the background sulfate concentration was about $0.5 \mu\text{g}/\text{m}^3$. In contrast, the bromide is clearly traffic-related.

No acidity was detected on the filters by Gran titration. Studies on techniques to preserve the acid on filters revealed that neutralization could have occurred during transport or handling prior to the acid measurements. Procedures to protect aerosol samples from being neutralized during handling have now been perfected.

The sulfuric acid monitor (SAM) from Cabot Corporation had just been constructed a few days before the study began and required several major modifications. The sampler and analyzer combination proved impractical and it was decided to operate the SAM as an analyzer only. Samples would be collected with the LBL and the trichotomous samplers. Due to day-to-day variations in calibrating the SAM, uncertainties of $0.5 \mu\text{g}/\text{m}^3$ sulfuric acid were typical with this prototype instrument. The best SAM data were obtained from the LBL dichotomous samplers, but these filters were submitted to the SAM only early in the program. The mean daily difference between the background sulfuric acid and the in-roadway LBL samples was $0.12 \mu\text{g}/\text{m}^3$. Sulfuric acid measurements on samples collected with the trichotomous sampler also showed about the same differences between background and in-roadway.

E. Summary of Results

The measurements made during these studies in Los Angeles show that the sulfate concentrations on roadways due to catalyst-equipped automobiles are small enough in comparison with background sulfate concentrations that they are generally obscured by the scatter in the analytical data. On a clear day (low background sulfate) with good ventilation, the sulfate increase due to catalyst cars was still not clearly seen, but was almost certainly below $1 \mu\text{g}/\text{m}^3$. Table 8 is a summary of measurements made on October 21, 1976, showing the sulfate differences with all the measurement methods and is typical of the results obtained during the study.

F. Conclusions and Planned Work

This study has demonstrated the feasibility of determining in-roadway levels of vehicle-emitted sulfate by making measurements using sampling and analysis equipment installed in vehicles moving on the roadway. There is no reason to believe that this technique would not be applicable to other aerosol or gaseous pollutants.

TABLE 7

Small Particle Sulfate Differences
Daily Averages of Data from the LBL Dichotomous Samplers

<u>Date - October 1976</u>	<u>Average Freeway Concentration $\mu\text{g}/\text{m}^3$</u>	<u>Average Background Concentration $\mu\text{g}/\text{m}^3$</u>	<u>Difference $\mu\text{g}/\text{m}^3$</u>
19	13.16	13.19	-0.03
20	15.23	17.03	-1.80
21	6.71 ^(a)	8.37	-1.66
21	8.77 ^(b)	8.37	+0.40
22	8.21	7.50	+0.72
24	8.22	11.73	-3.51
25	8.81	11.97	-2.16
26 ^(c)	0.40	0.67	-0.27
27 ^(c) a.m.	1.50	1.02	+0.48
27 ^(c) p.m.	0.98	0.71	+0.27

(a) Average includes filter 202 with $0.5 \mu\text{g}/\text{m}^3$ sulfate.

(b) Average omits filter 202.

(c) Only one freeway and one background sample analyzed.

TABLE 8
Freeway-Background Sulfate Differences
Observed on October 21, 1976

Collection Method	Analytical Method	Daily Average		Difference F-B	Units	Sulfate Difference $\mu\text{g}/\text{m}^3$
		Freeway	Background			
LBL Dichot.	SAM	1.24	0.91	0.33	$\mu\text{g}/\text{m}^3 \text{H}_2\text{SO}_4$	0.3
Two-Mass (WU)	FV-FPD ^(c)	3.04	2.27	0.77	$\mu\text{g}/\text{m}^3 \text{S}$	2.3
Two-Mass (WU-CIT)	FV-FPD	3.04	2.67	0.38	$\mu\text{g}/\text{m}^3 \text{S}$	1.1
LBL Dichot.	Ion Chrom.	8.77	8.37	0.40	$\mu\text{g}/\text{m}^3 \text{SO}_4^{=}$	0.4
LPI (UM) ^(a)	FV-FPD	2.20	2.31	-0.10	$\mu\text{g}/\text{m}^3 \text{S}$	-0.3
LPI (UM) ^(b)	FV-FPD	0.29	0.16	0.13	$\mu\text{g}/\text{m}^3 \text{S}$	0.4
LPI (UM-CIT) ^(b)	FV-FPD	0.29	0.20	0.09	$\mu\text{g}/\text{m}^3 \text{S}$	0.3
Mean						0.6
Standard Deviation						0.8

(a) All stages of the low pressure impactor.

(b) Stages 7 and 8, which nominally collect particles 0.02 to 0.11 μm in diameter

(c) FV-FPD = Flash Volatilization - Flame Photometric Detector

While data were obtained for only a few days, the levels of sulfate from catalyst-equipped vehicles (estimated to be 30% of all vehicles) were so low that there seems to be no reason for conducting a larger scale study next year. The lower-than-expected sulfate emission factors found in a surveillance study of in-use vehicles reported in Section IV. B., above, supports this conclusion.

It is planned to conduct a small-scale in-roadway study to assess an extreme worst-case situation. This is called the "cluster experiment." It is designed to determine the levels of sulfate to which vehicle occupants would be exposed if they were driving immediately behind a cluster of several high-sulfate-emitting vehicles. Such high-sulfate-emitting vehicles have been shown in the surveillance study cited above to constitute a small percentage of the in-use vehicle population. If this experiment indicates high levels of sulfate from the "cluster" we will ask the statisticians to estimate the probability of occurrence of this worst case.

V. MODELING

Development of theory adequate to quantitatively describe the transport of sulfuric acid mist from catalyst-car tailpipes to the exposed population has been concentrated during the past year on dispersion and aerosol coagulation processes.

The Meteorology and Assessment Division of ESRL has conducted a variety of tests of the current Gaussian plume model of a line-source roadway (the HIWAY model) using long-time-scale data from the GM proving ground experiment. The tests so far clearly indicate the current procedure -- that of assigning overall Gaussian distribution parameters on the basis of wind stability alone -- leads to overestimation of ambient air sulfuric acid mist concentrations under conditions of poor atmospheric dispersion. Follow-on efforts, which seek to improve the predictive capability of this simple theory, involve extraction of best-fit Gaussian distribution parameters from the short-time-scale GM data. However, the data have only recently been received by EPA and these calculations will continue into early FY-78. At this point, the mechanical source of predictive error might be either inability to account for short-term wind meander under conditions of low wind speed or to non-Gaussian concentration profiles induced by motion of the cars.

More complicated models are also being tested in the hope that inclusion of greater physical detail will improve predictive capability. One such approach involves numerical integration of point sources to produce a better description of the roadway as a line source. The techniques and computer programs for performing these calculations have been developed during the past year. Testing of this procedure will be accomplished in future work.

Another, still more complicated, method summarizes overall roadway dispersion by following the mechanical and chemical transformations of individual parcels of air. A contract to develop this Lagrangian model has been initiated in FY-77. Still another approach involves handling the mathematical expressions describing the variety of mechanical influences on air motion (wind effects, advection, automobile-induced turbulence) as essentially additive. Integration of these effects by the finite difference approximation can then produce an overall view of the roadway. This procedure has been tested using the long-time-scale GM data base during the past year and does represent a significant improvement over the simpler HIWAY model.

While the GM data base has proven valuable in preliminary testing of dispersion models, it is very limited. Only a few conditions of wind speed, direction, and stability occurred in the atmosphere during the short time of the experiment. A much more extensive set of data is being obtained in an ESRL-supported study on the Long Island expressway cooperative with the New York State Department of Environmental Conservation. Nine months of SF_6 dispersion data are now available from the study and workup of wind field, energy balance, and aerosol composition data is in progress. It is expected that this new data will allow much more accurate and complete evaluation of various models and determination of specific problem areas in prediction.

An important addition to our ability to assess pollution problems associated with roadway-produced aerosols is the development of theoretical procedures sufficient to determine effects of aerosol growth, deposition, and chemical reactions on exposures. Recent work carried out by ESRL-Aerosol Research Branch has shown that the ultrafine sulfuric acid aerosols found in the GM track experiment must persist in the size range for significant time intervals as sulfuric acid. Only insignificant neutralization, growth can occur over a roadway. Hence, motorists must be exposed primarily to sulfuric acid.

The value of the predictive ability represented by these physical and chemical mathematical procedures is very great. Changes in automotive and fuel technology are occurring rapidly in response to pollution control and energy conservation challenges. Since these changes can frequently induce new requirements for quick assessment of environmental impact, we expect models developed here to be applied to new problems with some regularity in the next few years.

MONITORING PROGRAM FOR CATALYST-GENERATED SULFURIC ACIDINTRODUCTION

As a consequence of the deferral of the sulfuric acid standard for MY-79 cars, a surveillance program has been proposed to monitor sulfuric acid concentrations on and near roadways. The purpose of this surveillance is to measure concentrations of automobile-generated sulfuric acid to determine whether it is necessary to take action to prevent sulfuric acid concentrations from reaching levels that would constitute a hazard to public health. California has been chosen as the most suitable area for surveillance since projected sulfuric acid concentrations there should precede those in major urban areas in the rest of the U.S. by two or three years.

Past experience dictates that the highest and therefore controlling concentrations will occur on freeways. Therefore, emphasis should be placed on measurement of sulfuric acid concentrations on or immediately adjacent to such roads with high vehicle densities.

Two general measurement approaches have been considered. The first employs measurements on the road with monitors situated in vehicles moving along a road segment (e.g., measurements on the Milford test track); the second uses fixed sites adjacent to roads and measures differences in concentrations across the roads. These differences are then attributed to sources on the roads (e.g., the LACS program). Each approach has its advantages and disadvantages, and an abundance of proponents to express their views in the forthcoming meetings which will address the details of a suitable surveillance program.

While considerable technical discussion is taking place relative to suitable measurement techniques to detect catalyst-generated sulfuric acid in ambient air, an equally important subject has received less attention. This is the design of a combined sampling and simulation program that produces estimates of population exposure to catalyst sulfates. Whatever the nature of the roadway measurements, they do not necessarily convey information on the distributions of concentrations and exposures. They do so only when they are employed within a sampling and/or simulation framework that permits inferences concerning the distributions of human exposures. This point seems to have been somewhat neglected to date.

To underscore this aspect of the proposed surveillance program, we would like to briefly discuss three ways of inferring distributional information that have emerged from our own thinking and from discussions at NPRM committee meetings.

These are:

- (1) Estimation of the n-th highest concentration over the roadway network of interest. This method is analogous to the procedure used to establish emission increments or decrements for AQCR's in SIP's.
- (2) Estimation of the probability distribution of sulfuric acid concentrations on a roadway network.
- (3) Estimation of the probability distribution of sulfuric acid exposures to travelers on a roadway network.

(1) n-th Highest Concentration Method

In this method, we pick the roadway network of interest (e.g., all Los Angeles freeways). Decisions on whether to control further growth in sulfuric acid emissions would be determined by comparing the measured n-th highest concentrations on the network (e.g., the second highest) to a reference concentration that could not be exceeded.* Such an approach would be analogous to the approach currently used in SIP's for criteria pollutants.

There are two difficulties with this approach -- one theoretical and one practical. The theoretical difficulty is that the concept of a threshold value not to be exceeded more than n-1 times per year has no statistical meaning. The number of times a threshold value is exceeded is a random variable that depends on such things as traffic and meteorological conditions. There exists no fixed concentration that is certain to be exceeded exactly n-1 times per year. Any control decision based on the n-th highest value, therefore, is certain to be either too stringent or too lenient.

The theoretical difficulties of the n-th highest concentration approach have not been acknowledged formally by EPA, owing in part to the disruptions in the SIP process that such an acknowledgement might cause. However, the theoretical problems are recognized informally. They are the reason for many prolonged and inclusive discussions over how to select a base year for rollback modeling (e.g., how one knows that pollutant concentrations in a particular year are not unusually high or unusually low).

*This, of course, assumes that the health effects people will be able to define a concentration that corresponds to the onset of significant adverse health effects prior to the time such concentrations will be achieved at frequencies of concern.

The practical problem with the n-th highest concentration approach is that there are a large number of sampling sites at which this value might occur. With sufficient knowledge of the relevant conditions, one presumably could eliminate most of these sites as being unlikely locations for the occurrence of the n-th highest values, and monitoring could be conducted only at a relatively small number of "high-concentration" sites. However, we believe that great practical difficulties would be encountered in attempting to identify a suitable set of high-concentration sites within the freeway network. Complicating factors of wind angle relative to the road, and highly variable vehicle-average emission factors (and total emission rates) associated with local driving conditions and vehicle flowrates could make the identification of these sites extremely elusive. Moreover, the shorter the averaging time chosen, the greater the difficulty that will be encountered in identifying the n-th highest concentration. Both the cost and time period required to identify suitable monitoring sites could be substantial. It would be necessary to acquire sufficient monitoring data to choose a small number of sites out of a much larger set of candidate sites. It is likely that annual frequency distributions of sulfuric acid concentrations at many potential sites (e.g., tens or hundreds of sites) could be needed to establish the monitoring network.

The problem of selecting suitable monitoring sites, like the problem of the meaningless n-th highest value threshold, has been recognized informally in discussions of SIP's. In the SIP's, the siting problem is the cause of questions about whether an existing monitoring network corresponds to pollution "hot spots." It also is the source of the frequent observation that when a monitoring network in an AQCR is expanded, measured concentrations of some pollutants increase.

(2) Estimation of the Probability Distribution of Sulfuric Acid Concentrations on a Roadway Network

In this method, we pick a roadway network of interest and construct an estimate of the cumulative probability distribution of sulfuric acid concentrations over the entire network.

The decision variable which can be obtained from this distribution is a specified percentile concentration, representative of upper bound on concentrations which would be experienced by a large fraction of travelers on the network. This high percentile concentration (as in the case of the n-th highest concentration) is compared to a given threshold concentration to determine whether further growth in sulfuric acid emissions must be controlled.

There are two methods for obtaining an estimate of the probability distribution of roadway concentrations on the network. Each calls for a substantially different monitoring program.

(a) Direct Measurement Method

In this method, sulfuric acid concentrations would be measured at randomly selected sites and times on the network of interest. The measured concentrations would be used to estimate the probability distribution of sulfuric acid concentrations on the network. There would be no need for an air quality simulation model and statistically meaningful estimates of the features of the probability distribution of sulfuric acid concentrations would be obtained. The method would require a carefully conducted random sampling program. Monitors would have to be sufficiently mobile to obtain random samples over the entire freeway/highway network.

The accuracy with which the features of the distribution of sulfuric acid concentrations could be determined through sampling depends on which specific features are of interest, the size of the sample, and, in some cases, the probability distribution function of sulfuric acid concentrations. For example, suppose the sample size is 1000 per year and one is interested in percentiles of the distribution of sulfuric acid concentrations on freeways. The computations with the HIWAY model suggest that the distribution of sulfuric acid concentrations on freeways is approximately exponential. With an exponential distribution, a random sample of size 1000 would establish the 99th percentile with an accuracy of about $\pm 5 \mu\text{g}/\text{m}^3$ at the 95 percent confidence level. For the 95th percentile, the accuracy would be $\pm 2 \mu\text{g}/\text{m}^3$. For the median it would be $\pm 2 \mu\text{g}/\text{m}^3$.

An alternative approach would be to use sampling to estimate the probability that freeway sulfuric acid concentrations exceed some threshold value. A sample size of 1000 would establish such a probability with an accuracy no worse than $\pm .03$ with 95 percent confidence. The accuracy would be better at threshold values that have relatively low probabilities of being exceeded.

(b) Combined Measurement and Simulation

In this method, average sulfuric acid emissions factors would be estimated from measurements of roadway sulfuric acid concentrations. These emissions factors then would be used in connection with an air quality simulation model to develop frequency distributions of sulfuric acid concentrations. In effect, this method would recompute the existing concentration estimates using a better estimate of the emission factor.

The principal advantage of this approach is that it might require a smaller sample than the direct measurement approach, because meteorological variables would be handled with the simulation model,

thus reducing the variability in the data. However, the approach would involve all the upper bounding arguments, approximations, and issues of model accuracy that are already present in the existing concentration and exposure estimates.

(3) Estimation of the Probability Distribution of Sulfuric Acid Exposures to Travelers on a Roadway Network

In this method, either of the concentration distributions of the preceding method would be used simultaneously with travel time data on the same freeway/highway network to construct cumulative probability distributions of traveler exposures on the freeway/highway network.

The decision variable from either of the two exposure distributions would be a specified percentile exposure measured as a time-averaged sulfuric acid concentration. Again, either of these exposure parameters could be compared to a preassigned threshold value of exposure to determine when further growth in sulfuric acid emissions must be controlled.

(a) Direct Measurement Method for Exposure Distributions

In this method we would construct a concentration probability distribution by method (2-a). We would then place this distribution in the current algorithm which uses it along with travel time data to produce a cumulative probability distribution of traveler exposures. A preassigned percentile exposure can then be compared directly with a threshold value of exposure to determine whether control actions should be taken.

(b) Combined Measurement and Simulation Method for Exposure Distributions

In this method we would construct a concentration probability distribution by method (2-b), and proceed as in method (3-a).

CONCLUSIONS

We consider the direct measurement approach using random sampling methods (2-a) or (3-a) to be superior to the other two monitoring approaches described here. The recommended approach:

1. Relies on statistically meaningful quantities.
2. Is relatively free of problems of site selection.
3. Does not require the use of air quality simulation models.
4. Produces data which can be used to form a variety of policy-oriented indicators of sulfuric acid concentrations and exposures.

In contrast, the n-th highest concentration approach does not have advantages 1 or 2 above, and the measurement/simulation approach [methods (2-b) or (3-b)] does not have advantage 3.

If, for some reason, the recommended approach cannot be adopted, then we believe the combined measurement/simulation approach should be used. Next to the recommended approach, the measurement/simulation approach would have the fewest disadvantages -- particularly if an improved air quality simulation model is developed. We would advise against using the n-th highest concentration approach. It cannot produce statistically meaningful results; it cannot produce results that can be compared with the existing exposure/concentration estimates; and it has severe practical problems.

If the combined measurement and simulation approach is used in either methods (2) or (3), it may be a good idea to replace the HIWAY model by an Air Quality Simulation Model (AQSM) which more accurately simulates the physical processes of dispersion and convection at wind speeds, wind angles, and stability conditions leading to the higher pollutant concentrations. Results of the Milford test track experiment support previous evaluations of the HIWAY model. These results show that the HIWAY model performs poorly (or at best indifferently) at low wind speeds, at low atmospheric diffusivity and when the wind is nearly parallel to the road. Each of these factors separately contributes to increased concentrations. When they exist simultaneously they produce the highest concentrations at a fixed emission density and roadway geometry. But the high concentration ranges predicted by the AQSM must be accurately represented since they constitute the most likely regions for use in decisions to initiate control actions.

One final note on model development and validation is in order, since there appears to be some confusion on its role relative to the monitoring program discussed above. New model development, calibration and validation would not employ the data collected in the measurement program on the freeway and highway networks mentioned above. Use of that data for the development of concentration frequencies on the freeway and highway networks requires the existence of an accurate air quality simulation model, which has been calibrated and validated against data sets developed independent of the freeway/highway network measurements. This does not mean that the validation data could not be collected on the same network -- in fact, that would probably be the best place to collect it. However, the validation data-gathering exercise here would constitute an entirely independent activity.

APPENDIX B-2

ESTIMATE OF PROBABILITY DISTRIBUTION OF ONE-HOUR AVERAGE EXPOSURES TO AUTOMOBILE-GENERATED SULFURIC ACID FOR MORNING PEAK PERIOD TRAVELERS IN LOS ANGELES

INTRODUCTION

One of the problems involved in the development of a sulfuric acid emissions standard for new cars is the estimation of the sulfuric acid exposures that would result from various levels of automobile emissions of sulfuric acid. This problem has been addressed in previous EPA papers (Ref. 1, 2, 3), and estimates of "typical" and "worst case" exposures to automobile-generated sulfuric acid for various emissions scenarios have been presented. These estimates place bounds on the range of sulfuric acid exposures likely to be experienced as a result of sulfuric acid emissions from cars. However, the estimates provide no information about the probability of occurrence of various levels of sulfuric acid exposure. Thus, for example, the estimates cannot be used to answer questions such as: what is the probability that 1-hour average exposures will exceed $15 \mu\text{g}/\text{m}^3$ if cars emit sulfuric acid at a specified rate?

The failure of the previous estimates to answer questions of this kind significantly constrains their usefulness. The "worst case" estimates are based on the simultaneous occurrence of various rare events (e.g., prolonged periods of travel on high-volume freeways under meteorological conditions conducive to the formation of unusually high concentrations of pollutants) and, therefore, may represent exposure levels that are too unlikely to be of practical importance. On the other hand, the "typical case" exposure estimates provide no information about the reasonable extremes of exposure and, thus, cannot be used in developing policies to protect people from these extremes.

This paper provides an estimate of the probability distribution of short-term (1-hour average) exposures to automobile-generated sulfuric acid for a particular urban sub-population, namely weekday morning peak period travelers in Los Angeles. The choice of Los Angeles as the city for which the probability estimates were made was dictated by data availability; Los Angeles is the only city in the U.S. for which the required data were readily available. The estimates were made for the weekday morning peak period (6-9 a.m.) because the traffic and meteorological conditions that occur during the period tend to cause 1-hour average concentrations of automobile-generated sulfuric acid to be higher during this period than at other times (Ref. 4). Thus, weekday morning peak period 1-hour-average exposures to automobile-generated sulfuric acid are likely to be higher than 1-hour exposures experienced at other times. The probability estimates were made for morning peak-period travelers only. This sub-population includes roughly 30 percent of the total Los Angeles population. The excluded sub-population, persons who do not travel in the morning peak, will be addressed in a subsequent paper.

EMISSIONS FACTORS

At present, techniques for measuring sulfuric acid emissions from automobiles are not fully developed. Consequently, sulfuric acid emissions from current catalyst cars cannot be estimated with precision. Therefore, the exposure estimates presented in this paper are based not on current measured sulfuric acid emissions by catalyst cars, but on a set of plausible (but hypothetical) sulfuric acid emissions factors. The assumed emissions factors are 0.010 g/mi for cars on city streets and 0.035 g/mi for cars on freeways. Although these emissions rates are hypothetical, it is likely that they could be achieved by cars equipped with catalysts if emissions standards were established at the appropriate levels. The exposure estimates assume that all cars in use emit sulfuric acid at these rates.

Data

Two types of data were used in constructing exposure estimates: travel data and meteorological data. The travel data were obtained from the 1967 Los Angeles Regional Transportation Study (LARTS). These data consisted of records of 36,733 trips made during the weekday morning peak period (6-9 a.m.) in the Los Angeles area and estimates of the time spent on freeways and city streets during each trip. 1967 is the only year for which these data are available.

The meteorological data consisted of hourly observations of wind speed, wind angle, and stability class at Los Angeles International Airport during the 6-9 a.m. period of each day during 1964. 1964 is the only year and Los Angeles International Airport the only site for which suitable meteorological data were available. Meteorological conditions tend to vary somewhat from year to year; in some years, conditions are conducive to higher concentrations of pollutants than in other years. Conditions in 1964 were roughly in the middle of this range and were not conducive to forming either unusually high or unusually low concentrations of pollutants (Ref. 4, 5).

Methodology

The travel data were used to construct the joint frequency distribution of travel time on city streets and freeways during the hour following the start of a morning peak period trip in the Los Angeles area. Some features of this travel time distribution are shown in Table 1. The travel time distributions are skewed to the right. This means that travel times are relatively short for most travelers but are long for a few travelers. For example, 55 percent of peak period travelers do not use freeways at all during the hour following the start of a morning peak period trip. However, one percent of travelers are on freeways for at least 56 minutes during the hour following the start of a trip.

The meteorological data were used together with the HIWAY diffusion model (Ref. 6) to construct the joint frequency distribution of 1-hour average concentrations of automobile-generated sulfuric acid on city streets and freeways in the Los Angeles area during the 6-9 a.m. period. These concentrations represent increments over the general background level of automobile-generated sulfuric acid. In performing this calculation, traffic volumes of 3200 vehicles per hour on city streets and 17,000 vehicles per hour on freeways were assumed. These volumes correspond to observed peak-hour traffic flows on heavily-traveled streets and freeways in Los Angeles (Ref. 7). The sulfuric acid concentrations obtained from HIWAY were divided by two to correct for the observed tendency of HIWAY to over-predict concentrations by roughly a factor of two on the average (Ref. 8). It was assumed that sulfuric acid emitted by cars is not removed from the atmosphere by chemical reactions or other means during the time period being modeled.

Some features of the frequency distribution of concentrations are displayed in Table 2. Histograms of the marginal distributions are shown in Figures 2 and 3. The concentration distributions, like the travel time distributions, are skewed to the right. Thus, the peak period one-hour average sulfuric acid concentrations on freeways can be as high as $290 \mu\text{g}/\text{m}^3$, but 99 percent of the time it is less than or equal to $40 \mu\text{g}/\text{m}^3$. On city streets, the sulfuric acid concentration can reach $22 \mu\text{g}/\text{m}^3$, but 99 percent of the time it is less than or equal to $4 \mu\text{g}/\text{m}^3$.*

For fixed values of city street and freeway travel times and sulfuric acid concentrations, sulfuric acid exposure during the hour following the start of a peak period trip was computed as follows:

$$(1) \text{ EXP} = C_f T_f + C_s T_s + B$$

where:

EXP = One-hour average exposure to sulfuric acid

C_f = One-hour average sulfuric acid concentration on freeways (increment over background)

C_s = One-hour average sulfuric acid concentration on city streets (increment over background)

T_f = Time spent on freeways (in hours) during the hour following the start of a trip

T_s = Time spent on city streets (in hours) during the hour following the start of a trip

B = Sulfuric acid background due to sulfuric acid emissions from cars

*These concentrations represent increments over the general background level of automobile-generated sulfuric acid.

The background sulfuric acid concentration, B , was estimated using a simple box model and was found to be less than $1 \mu\text{g}/\text{m}^3$. However, for computational reasons, background was set at $1 \mu\text{g}/\text{m}^3$ when performing the exposure computations.

The probability distribution of EXP was computed from Equation (1) by allowing C_f , C_s , T_f , and T_s to be random variables with the previously discussed probability distributions for concentrations and travel times.

RESULTS

EXP estimates the one-hour average exposure to automobile-generated sulfuric acid during the hour following the start of a weekday morning peak period trip in the Los Angeles area. There were approximately 10^9 such trip starts in Los Angeles in 1967, the year of the LARTS survey.

Significant features of the probability distribution of EXP are displayed in Table 3. Figure 4 shows a histogram of EXP. The distribution of EXP is skewed right and has a very long tail. EXP can reach a level of $290 \mu\text{g}/\text{m}^3$ (the worst case). However, the 99th percentile of EXP is $12 \mu\text{g}/\text{m}^3$, and the median value of EXP is less than $2 \mu\text{g}/\text{m}^3$.

The values of EXP shown in Table 3 and Figure 4 as well as the concentrations in Table 2 and Figures 2 and 3 were computed for a specific set of sulfuric acid emissions factors, namely $0.010 \text{ g}/\text{mi}$ on city streets and $0.035 \text{ g}/\text{mi}$ on freeways. Exposures and concentrations for other sets of emissions factors with the same ratio of freeway to city street emissions can be obtained by linear scaling. Thus, the exposures and concentrations would be double those shown in emissions were $0.020 \text{ g}/\text{mi}$ on streets and $0.070 \text{ g}/\text{mi}$ on freeways. The concentrations and exposures would be half those shown in emissions were $0.005 \text{ g}/\text{mi}$ on streets and $0.0175 \text{ g}/\text{mi}$ on freeways.

SOURCES OF ERROR IN THE ESTIMATES

The exposure estimates are subject to two types of error: systematic biases and random errors. Systematic biases create errors in the estimated exposures to be mostly too high or mostly too low. Random errors cause the estimated exposures to be sometimes too high and sometimes too low but correct on the average.

The principal sources of systematic bias in the results presented here are the street and freeway traffic volumes used to estimate sulfuric acid concentrations. These traffic volumes tend to cause the estimated sulfuric acid concentrations and exposures to be too high, because traffic volumes on most street and freeway segments are not as great as

the volumes used in developing the estimated concentrations. Another possible source of systematic bias is the absence of sulfuric acid removal mechanisms in the HIWAY model. If chemical reactions with atmospheric ammonia or other mechanisms remove significant quantities of sulfuric acid from the atmosphere over the period of one hour, the estimated exposures again would tend to be too high.

The principal source of random error in the estimates is the random error of the HIWAY diffusion model. This model, like other diffusion models, produces concentration estimates that can be too high or too low by up to a factor of roughly two. This factor of two is distinct from the HIWAY model's tendency to systematically overestimate concentrations by a factor of two. The latter source of error was removed in the estimation procedure. In addition, all of the travel and meteorological data used in developing the exposure estimates are subject to random error. The most significant source of random error in these data may be the use of instantaneous hourly meteorological conditions at Los Angeles International Airport to represent hourly average conditions over the entire Los Angeles area.

It is not possible to estimate the magnitudes of the various errors in the exposure calculations. As a guess, it is possible that the systematic biases might cause the exposure estimates to be too high by as much as a factor of two and that the random errors might cause the estimates to be too high or too low by a factor of two to three.

COMPARISON WITH PREVIOUS RESULTS

A previous EPA summary and evaluation of sulfuric acid exposure levels (Ref. 3) concluded that if cars emitted 0.030 g/mi of sulfuric acid on freeways, then peak 1-hour exposures of urban commuters to automobile-generated sulfuric acid "are not likely to exceed $127 \mu\text{g}/\text{m}^3$ except under very rare conditions, when exposures could reach $208 \mu\text{g}/\text{m}^3$." When adjusted to reflect the 0.035 g/mi freeway emissions factor used in the present paper, the earlier paper's conclusion becomes: 1 hour sulfuric acid exposures are not likely to exceed $148 \mu\text{g}/\text{m}^3$ except under rare conditions, when exposures could reach $243 \mu\text{g}/\text{m}^3$. As explained in the introduction to the present paper, the prior exposure estimates did not include quantitative estimates of the likelihood of various exposure levels. The probability distribution developed in this paper indicates that the probability of a 1-hour exposure equal to or greater than $148 \mu\text{g}/\text{m}^3$ is roughly 3.5×10^{-6} . The probability of an exposure equal to or greater than $243 \mu\text{g}/\text{m}^3$ is roughly 10^{-6} .

CONCLUSIONS

The probability distribution of 1-hour exposures to automobile-generated sulfuric acid for weekday morning peak period travelers in the Los Angeles area has been estimated. The estimate is based on travel and meteorological data for Los Angeles. The results suggest that if cars emit 0.010 g/mi of sulfuric acid on city streets and 0.035 g/mi on freeways, then:

- Median 1-hour average exposure will be less than $2 \mu\text{g}/\text{m}^3$.
- Average 1-hour exposure will be $2 \mu\text{g}/\text{m}^3$.
- The 99th percentile of 1-hour exposures will be $12 \mu\text{g}/\text{m}^3$.
- The maximum 1-hour exposure will be $290 \mu\text{g}/\text{m}^3$ and will occur with probability 6×10^{-7} .

TABLE 1

FEATURES OF THE DISTRIBUTION OF TRAVEL TIME DURING
THE HOUR FOLLOWING THE START OF A MORNING PEAK
PERIOD TRIP IN LOS ANGELES^(a)

	<u>Time on Streets</u>	<u>Time on Freeways</u>	<u>Total Travel Time</u>
Average	11	6	17
Median	9	0 ^(b)	13
95th Percentile	29	32	52
99th Percentile	43	56	60
Maximum	60	60	60
Probability of Maximum	0.001	0.008	0.03

(a) Travel times are in minutes.

(b) 55 Percent of peak period travellers do not use freeways during the hour following the start of a trip.

TABLE 2
FEATURES OF THE DISTRIBUTION OF CONCENTRATIONS OF
AUTOMOBILE-GENERATED SULFURIC ACID ON
STREETS AND FREEWAYS IN LOS ANGELES^(a)

	<u>Concentration on Streets</u>	<u>Concentration on Freeways</u>
Average	1	7
Median	less than 2 ^(b)	5
95th Percentile	less than 2 ^(b)	19
99th Percentile	4	40
Maximum	22	290
Probability of Maximum	8×10^{-5}	8×10^{-5}

(a) Concentrations represent increments over background in $\mu\text{g}/\text{m}^3$ - one-hour average.

(b) $2 \mu\text{g}/\text{m}^3$ is 98th percentile.

TABLE 3

FEATURES OF THE DISTRIBUTION OF ONE-HOUR AVERAGE
EXPOSURES TO AUTOMOBILE-GENERATED SULFURIC ACID DURING THE HOUR FOLLOWING
THE START OF A PEAK PERIOD TRIP IN LOS ANGELES

	<u>Exposure^(a)</u>
Average	2
Median	Less than 2 ^(b)
95th Percentile	6
99th Percentile	12
Maximum	290
Probability of Maximum	6×10^{-7}

(a) Exposure in $\mu\text{g}/\text{m}^3$

(b) $2 \mu\text{g}/\text{m}^3$ is 67th percentile.

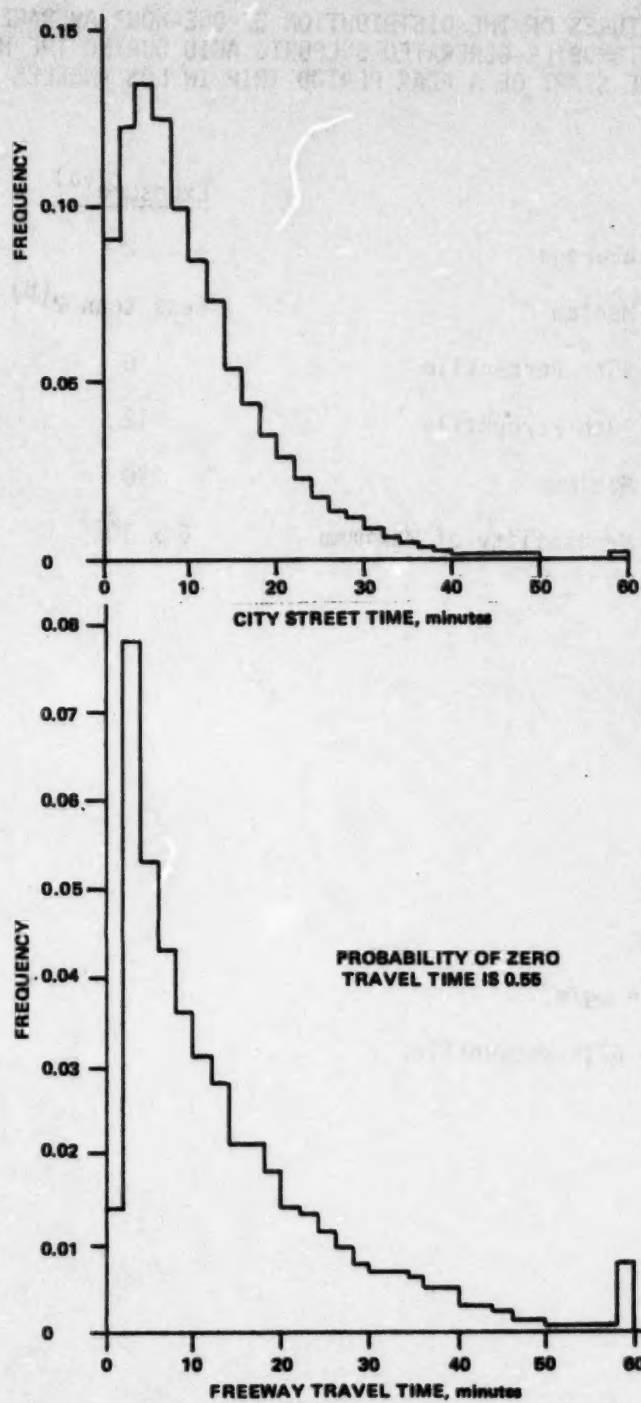


Figure 1. Histograms of freeway and city street travel times.

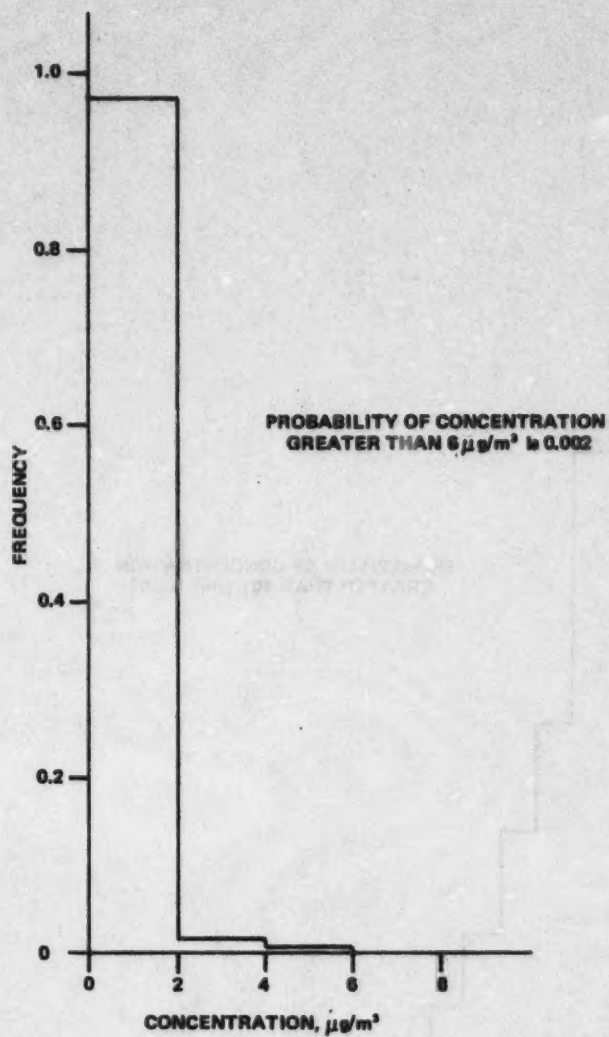


Figure 2. Histogram of city street sulfuric acid concentration, increment over background.

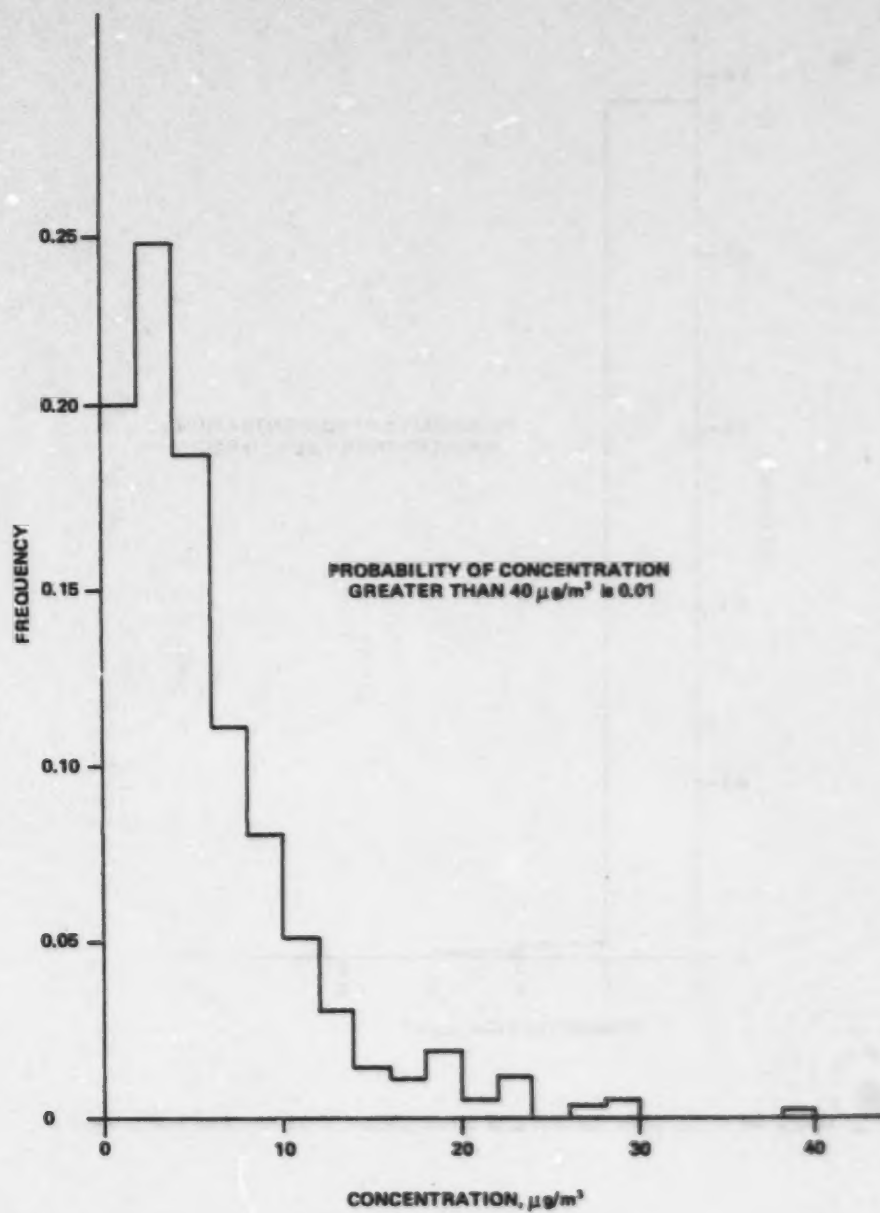


Figure 3. Histogram of freeway sulfuric acid concentration, increment over background.

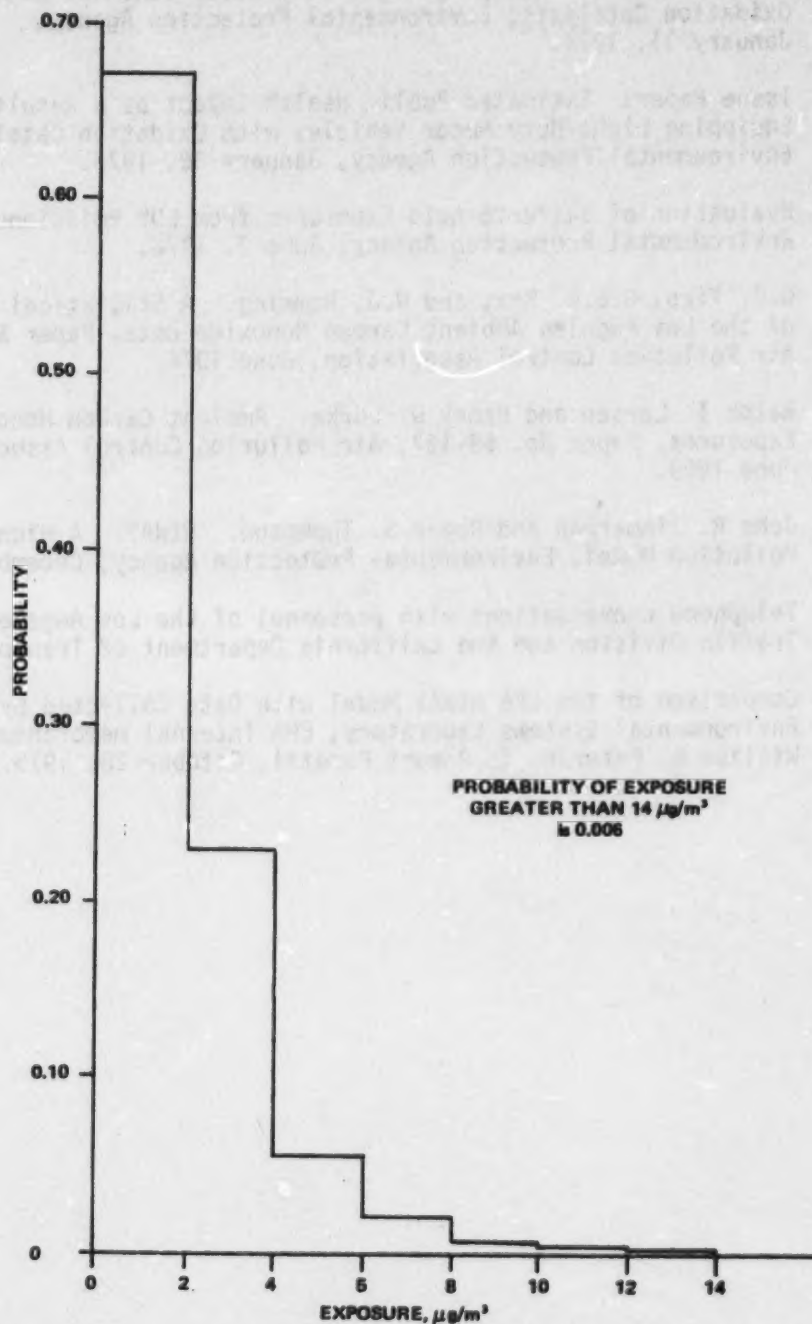


Figure 4. Histogram of EXP.

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APPENDIX C

THIRD ANNUAL CATALYST RESEARCH PROGRAM REPORT

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I. OVERVIEW

The Catalyst Research Program at the Health Effects Research Laboratory-Cincinnati, has been designed to provide EPA with biological data on the toxicologic effects of automotive emissions with and without the catalytic converter and on related single pollutants. In 1973, the Health Effects Research Laboratory-Cincinnati, began a series of studies in response to EPA's need for inhalation toxicology data on regulated and nonregulated emissions from oxidation catalysts. The HERL research effort was divided into two major segments: (1) assessment of the biological effects of automotive emissions which passed through the oxidative catalytic converter; (2) toxicological studies on single pollutants (noble metals, sulfates) associated with the oxidation catalyst. Data from these studies have been submitted in the annual Catalyst Research Program reports and have been published in the scientific literature. In the program for CY 1976, an additional study on the biological effects of catalytic emissions was planned in order to verify the findings of the previous catalytic emission study and to initiate investigations on the biological effects of ultrafine sulfuric acid. The initiation of the program for CY 1976 was delayed because of relocation to new facilities. Much time and effort was spent in moving and setting up new facilities and laboratory equipment.

A. Facilities

During CY '76, a new mobile emissions animal exposure facility was constructed at the EPA Center Hill Road laboratory. This facility replaces the Laidlaw facility which was used in previous studies. In the new facility, either gasoline or diesel exhaust can be generated independently and simultaneously. The facility will serve as a center for toxicologic screening, in relevant animal models, of potentially hazardous emissions derived from either gasoline or diesel automotive emissions. It thus provides for the assessment of the effects of the inhalation of non-irradiated and irradiated (artificial sunlight) automotive exhaust upon those biological parameters associated with general health and resistance to disease.

B. Research

The CRP plans at HERL-Cincinnati, can be categorized into four major areas of research. The areas involve the assessment of biological effects in laboratory animals following exposure to: (1) automotive catalytic emissions; (2) diesel emissions; (3) ultrafine sulfuric acid and metal sulfates; and (4) Mn compounds associated with the use of the additive MMT in gasoline. During CY '76, research was initiated in three of these areas--automotive catalytic emissions, diesel emissions, and metal sulfates.

1. Automotive Catalytic Emissions Study

A major research effort during late CY '76 was the initiation of a three-month exposure of laboratory animals to automotive catalytic-treated exhaust. Major emphasis was placed on defining the effects on pulmonary function. The exposure period has been completed and data are being analyzed. The reports should be completed in CY '77. After completion of this study, there are no immediate plans for additional animal exposures to automotive catalytic emissions.

2. Diesel Emissions Study

During the construction of the new Center Hill Road laboratory, arrangements were made to include a diesel capability in the facility. Installation and calibration of all of the necessary hardware required to operate the diesel engine is progressing satisfactorily and animal exposures to the exhaust will begin in CY '77. Major biological parameters to be investigated include effects on pulmonary function, histopathology and blood chemistry, biochemical alterations in the lung, and effects on spontaneous locomotor activity.

3. Ultrafine Sulfuric Acid and Metal Sulfates

Because of their presence in exhaust emissions of vehicles with catalytic converters, respirable aerosols of sulfuric acid and metal sulfates (aluminum sulfate, platinum sulfate) were tested using various biological parameters. Work on the metal sulfates is continuing. The exposures to sulfuric acid were done using particle sizes larger than those in the ultrafine range. Experiments in the ultrafine range await development of a generation system capable of producing ultrafine particles. A generation system should become available during CY '77.

4. Manganese Oxide Studies

The possible toxicity of airborne manganese has become an issue of concern because of the potential widespread use of an organic manganese compound (methylcyclopentadienyl manganese tricarbonyl) as an antiknock agent in gasoline. Studies involving inhalation exposure to manganese will be initiated during CY '77. Major biological parameters of interest include pulmonary changes and neurological alterations. One problem that must be solved before initiation of the experiments involves verification of the chemical form of manganese found in automotive exhaust.

It should be noted that most of the work conducted in CY '76 was in-house; however, there was some contract research which supplemented in-house work on the biological effects following exposure to automotive catalytic-treated emissions and the effects of exposure to sulfuric acid. This work has been incorporated into the report.

II. BACKGROUND AND INTRODUCTION

The Health Effects Research Laboratory-Cincinnati feels that it is important to maintain a research program directed toward obtaining information that will lead to an improved understanding of the biomedical consequences of exposure to mobile source emissions. An additional stimulant for research on mobile source emissions is the recognition that the Agency needs a research system which allows exposure to total emissions of alternative power and emission control devices for determining potential health hazards.

Mobile emissions (automotive, diesel, etc.) are comprised of a complex mixture of interacting chemical substances of varying toxicities. The National Research Council document on Fuels and Fuel Additives for Highway Vehicles and Their Combustion Products states that hundreds of compounds are present in the emissions of fuel combustion and it is practically impossible to detect and measure each one for the purpose of toxicologic experiments. A number of the components which may pose hazards to human health have not yet been fully investigated. We believe that the generation of automotive or diesel emissions in the laboratory setting is a far better and more feasible simulation of the "real world" than can be achieved "synthetically" by mixing combinations of pure (single pollutant) compounds. The generation of whole exhaust requires careful control and characterization but it is more practical in this sense than the monstrous task of generating the number of single pollutants and combinations of these. It is a mistake to ignore the interactions of various components which affect toxicity and which cannot be assessed in single pollutant studies. The potential biological hazards which may result from potentiation, synergism and the various other interactions among all the exhaust components can only be assessed by exposure to the total emission. Whole exhaust studies should be regarded as a biological screen utilizing various animal models for detection of biohazards of complex mobile emissions. This is not to detract from single pollutant studies which should be emphasized and coordinated with whole emission studies.

When one considers the magnitude of human exposure and the size of the automotive industry, it seems rather logical to suggest that the Agency should have or support a mobile source emissions generation capability which permits exposure of laboratory animals to total emissions. It would appear that data on the effects of exposure to total emissions, as well as data from exposure to single components of the emissions, would be extremely useful in replying to inquiries from interested groups.

The Health Effects Research Laboratory-Cincinnati has the physical facilities for the inhalation exposure of laboratory animals to total automotive gasoline or diesel engine emissions and also to single pollutants. The automotive emissions generation and exposure system which had

been previously located at the Laidlaw Avenue building was moved in January 1976, to a laboratory on Center Hill Road and the exposure chambers used for single pollutant studies were moved to the Environmental Research Center. The installation of all equipment has been completed and all chambers are operational.

Current Research Activities and Rationale

1. Automotive Catalytic Emission Studies

Since the inception of the CRP, the major research emphasis of this laboratory has been to provide EPA with biological data on the toxicological effects of animal exposure to whole emissions from automotive engines equipped with and without the catalytic converter. A secondary aspect of the program involved studies on the metabolism and biological effects of noble metals (Pt and Pd) and other nonregulated pollutants (H_2SO_4) associated with the use of the catalyst.

Aerometry data from the use of the catalyst has shown a major decrease in the concentrations of carbon monoxide and total hydrocarbons in the exhaust. The use of the catalyst also caused a decrease in sulfur dioxide accompanied by an increase in sulfuric acid concentrations. Previous work conducted at HERL has shown that animals exposed to catalytically treated auto exhaust fared better healthwise than did analogous animals exposed to noncatalytic exhaust. However, since sulfuric acid has been shown to have a much greater irritant potency than sulfur dioxide, its effects could offset the benefit gained by a decrease in other pollutants. Thus an additional study was planned for CY '76 in which an engine-catalyst combination (California hardware package) known to produce high concentrations of sulfuric acid would be used along with increased levels of sulfur in the gasoline. The primary purpose of this study was the assessment of the effects on the respiratory system. In addition, the study was designed to study information on the possibility of animal adaptation to the test atmospheres. The study was initiated in CY '76 and results will be available in CY '77.

2. Automotive Diesel Emissions Study

As the initial concerns of the use of the catalyst have been delineated, some of the activities of the CRP have been focused into related areas of research. One of these areas involves studies on the possible hazards of exposure to diesel exhaust. Automotive manufacturers have indicated the intention of increasing the production of diesel-powered automobiles. With the increasing number of diesel automobiles, EPA, certainly will be asked about the hazards to health and well-being of man exposed to these emissions and may be required at some later date to develop health effects criteria for evaluating risk versus benefit. The biological data based on the health effects of diesel emissions is extremely limited and inadequate for assessing possible hazards associated with increased

exposure. The EPA has been engaged in the identification and characterization of the diesel exhaust components. With respect to emissions of regulated pollutants, diesel engines have lower emissions of carbon monoxide and hydrocarbons than gasoline engines. However, this is not the case with nitrogen oxides, where high combustion pressures inherent in the diesel result in high nitrogen oxide emissions.

The aspects of pollution most usually associated with diesel engines by the public include visible smoke and odors, of which the former has been regulated since 1970 engines built for service in heavy duty vehicles. Particulates emitted by diesel engines are largely carbonaceous material, a portion of which falls within the range of particle sizes visible to the human eye as smoke. Smoke is influenced strongly by the size distribution of the particles as well as their total mass; in fact, some approaches to smoke reduction (metallic fuel additives) will actually increase total particulate emissions on a mass basis. Particulate emissions from diesel-powered passenger cars are approximately 20-50 times higher than comparable passenger cars burning unleaded gasoline. Data also indicate that various organics are absorbed on the surfaces of these carbon particles. The toxicity of these organics will be influenced by the sites of deposition and clearance of the particulate. Little biological information is available on the deposition of diesel particulate in the lungs and this is a major area of emphasis in the diesel study.

The contribution of diesel automobiles to the emissions of sulfates, or sulfuric acid, are of interest in view of the considerable attention given this subject since the advent of catalyst cars. The range for sulfate emissions for diesel cars falls between the average catalyst car without air injection and the average catalyst car with air injection. Another fact that should be pointed out is that, whereas the sulfate emitted by catalyst cars is essentially all sulfuric acid, it is not known what types of sulfates are emitted by diesels, nor how much of it is sulfuric acid.

Initially, the major emphasis of the research approach will be in evaluating the major target organ--the lungs. The laboratory has extensive experience in assessing lung changes by pulmonary function, biochemical and histopathological approaches. Other biological parameters such as teratogenicity, mutagenicity, collagen formation, etc., have been considered and will be evaluated through extramural support. During the last quarter of CY '77, the first diesel emission exposures will be initiated. The primary objective of the first diesel emission study is to gather sufficient information for: (a) preliminary toxicological assessment of the atmospheres; and (b) development of a second more specialized protocol.

3. Ultrafine H₂SO₄ and Metallic Sulfates

The next major area of research involves the assessment of the biological effects of exposure to ultrafine H₂SO₄ and metallic sulfates. Automobiles equipped with catalytic converters emit ultrafine sulfuric acid. In order for EPA to evaluate the possible health risks associated with ultrafine H₂SO₄, animal exposure studies to ultrafine sulfuric acid are needed in order to compare with results of exposures to larger size H₂SO₄ particles. Amdur has used changes in pulmonary resistance of guinea pigs as a measure of irritant potency of sulfate salts. All of her studies were done using particle sizes of at least 0.1 μ or greater. The trend of her data suggests an increase in resistance with decreasing particle size (0.1 μ m - .43% increase in resistance/ μ gSO₄/m³ - 1.0 μ m - .20% inc. in resistance/ μ gSO₄/m³). All of these studies involved acute exposures and very little information is available on the effects of long-term low-level exposures. Questions arise as to the pathophysiological significance of the acute bronchoconstrictive response and whether adaptation occurs following chronic exposure. What are the long-term sequelae of low-level H₂SO₄ exposure?

This area of research involves exposures of laboratory animals for a longer duration (for example - 3 months) to sulfuric acid and measurement of pulmonary function, histopathological and biochemical changes. The toxicity of some of the metal sulfates will also be determined.

4. Manganese Oxide Studies

The possible toxicity of airborne manganese has become an issue of concern because of the potential widespread use of an organic manganese compound (methylcyclopentadienyl manganese tricarbonyl - MMT) as an antiknock agent in gasoline. In addition to its use in gasoline, MMT is used as an additive to fuel oil for inhibiting smoke formation and improving combustion in turbines. The widespread use of MMT would result in an increase in the concentration of Mn in the ambient air although the degree of environmental impact is not precisely known. Major contributors to atmospheric Mn include ferromanganese blast furnaces, incinerators, coal-fired power plants, and the burning of residual fuel oil. For six types of coal-fired plants, the concentrations of Mn emitted ranged from 60 to 400 μ g/m³.

Manganese is an essential trace element in all living things and is quite ubiquitous in its distribution in nature. While in trace amounts, Mn is beneficial, industrial exposure of man to various Mn compounds has been associated with two different clinical syndromes: manganous pneumonia and chronic Mn poisoning affecting the CNS. Manganese poisoning in man has been primarily associated with mining and processing of Mn ores and in use of Mn alloys in the steel and chemical industries. This, coupled with poor ventilation, provides the setting for most cases of chronic Mn poisoning in the literature. The lungs have been incriminated as the major portal of entry in cases of Mn intoxication in man. However, there is evidence that much of the inhaled Mn is transferred by the mucociliary ladder to the gastrointestinal tract from which it is either absorbed or eliminated.

Our studies are designed to examine changes in the lung and CNS effects. A major portion of the Mn experiments will consist of long-term (6 months to 1 year) inhalation exposure of laboratory animals to the appropriate oxide of manganese. The effects on the lungs will be assessed histopathologically, biochemically, and by using pulmonary function measurements. Any neurological impairment will be determined through behavioral tests and measurement of biochemical changes in neurotransmitters. Many of the symptoms of chronic Mn poisoning are similar to Parkinson's disease and both have as the basis of symptomatology abnormal functioning of the extrapyramidal system.

III. CURRENT STATUS

The program for CY '76 called for additional studies on the biological effects of inhalation exposure to automotive emissions and to initiate investigations on the biological effects on inhalation exposure to ultrafine sulfuric acid and metal sulfates. However, the initiation of the program for 1976 was delayed because of relocation to the new Environmental Protection Agency center and to the Center Hill laboratory. The construction and testing of the new mobile emissions animal exposure system was completed in mid-summer 1976.

A. Physical Facilities

Briefly, the entire engine exhaust is mixed with filtered and conditioned air in a dilution tube. Diluted exhaust from the tube enters a large volume mixing chamber and a portion passes through dynamic flow irradiation chambers (to simulate sunlight) and is then conducted to animal exposure chambers. The system also provides nonirradiated exhaust in the same concentration (directly from the mixing chamber) and filtered, conditioned, ambient air for control animal exposure. Figure 1 illustrates the flow and essential equipment in the diesel emission system. The gasoline emission system is duplicated except for the common sharing of the control air purifier and monitoring instrumentation. The major physical components of the facility are: air purifiers, engine dynamometers, mixing chambers, irradiation chamber, animal exposure chambers, and monitoring instrumentation.

1. Air Purifiers

There are three identical air purifiers and each supplies $21.2 \text{ m}^3/\text{min}$. (750 CFM) of CBR (chemical, biological, radiological) filtered and conditioned air to maintain the required temperature and relative humidity in the animal exposure chambers. Three units are required: one for dilution air for the gasoline engine exhaust, another for dilution air for the diesel engine exhaust, and one for the clean air (control) animal exposure chambers. The pneumatic controls are completely automatic once the outlet temperature and relative humidity changes when the hot and moist engine exhaust enters the system.

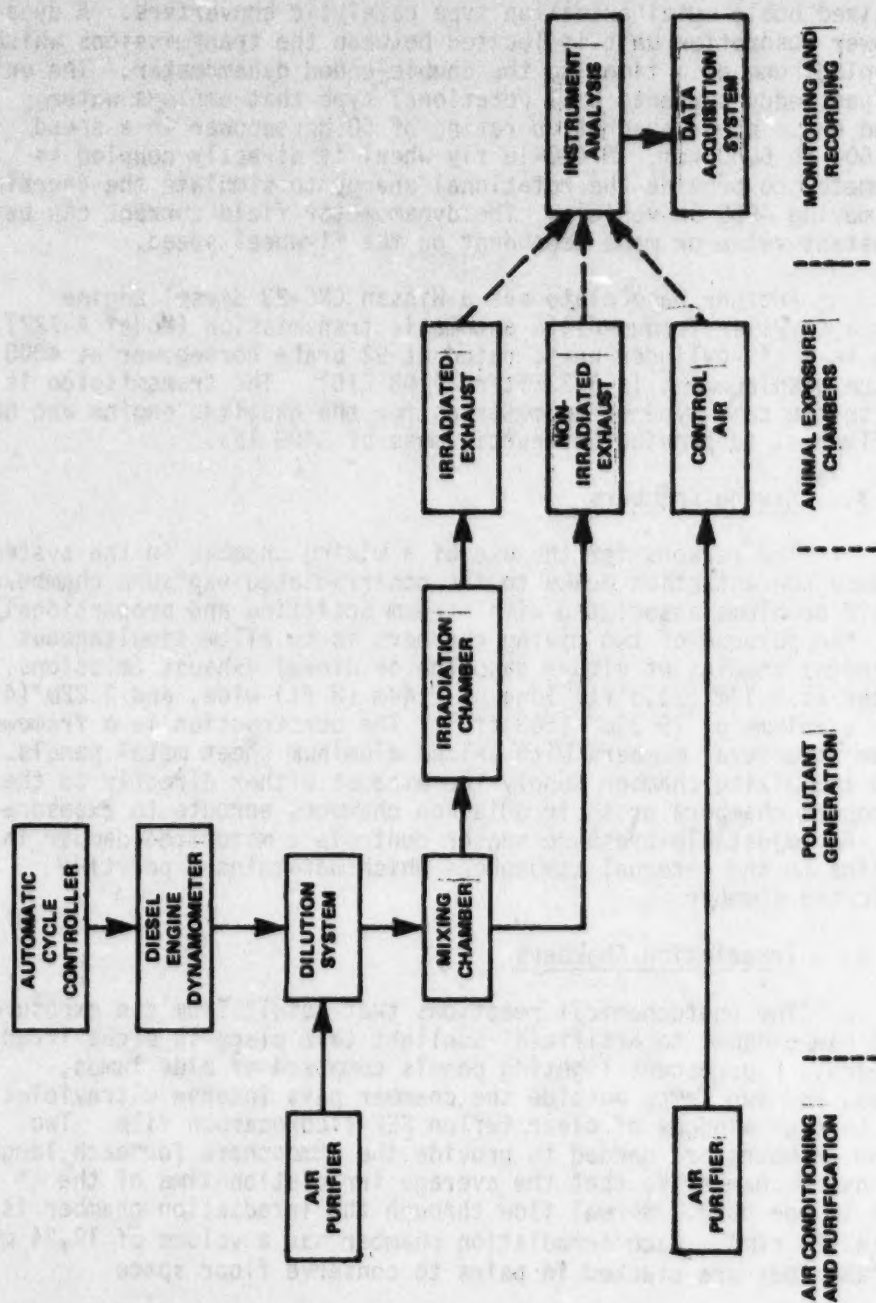


Figure 1. TADE project flow diagram: toxicological assessment of diesel emissions.

2. Engine Dynamometers

Mounted on one base plate are two 1975 General Motors 350 CID 8-cylinder gasoline engines equipped with automatic transmissions and pelletized noble metal oxidation type catalytic converters. A dynamometer power absorption unit is located between the transmissions which can be coupled, one at a time, to the double-ended dynamometer. The unit is an air gap, eddy current, dual rotational type that employs water cooling and has a power absorption rating of 50 horsepower in a speed range of 1600 to 6000 rpm. A 450-lb fly wheel is directly coupled to the dynamometer to provide the rotational energy to simulate the inertial mass of a moving 4000 lb vehicle. The dynamometer field current can be set at constant value or made dependent on the flywheel speed.

Another base plate has a Nissan CN6-33 diesel engine coupled to a Chrysler Torque-Flite automatic transmission (Model A-727). The engine is a six-cylinder unit, rated at 92 brake horsepower at 4000 rpm, and the displacement is 3.2 liters (198 CID). The transmission is connected to the same type dynamometer as for the gasoline engine and has a 300-lb flywheel to provide an inertia mass of 3400 lbs.

3. Mixing Chambers

The reasons for the use of a mixing chamber in the system are to reduce concentration peaks to the nonirradiated exposure chambers and to avoid problems associated with stream splitting and proportional sampling. The purpose of two mixing chambers is to allow simultaneous but independent studies of either gasoline or diesel exhaust emissions. Each chamber is 7.17m (23.5 ft) long by 2.44m (8 ft) wide, and 1.22m (4 ft) high, with a volume of 19.34m³ (683 ft³). The construction is a framework of aluminum structural members with welded aluminum sheet metal panels. Pipes from the mixing chamber supply the exhaust either directly to the animal exposure chambers or to irradiation chambers enroute to exposure chambers. An adjustable pressure sensor controls a motorized damper in the vent line to the external atmosphere which maintains a positive pressure in the chamber.

4. Irradiation Chambers

The photochemical reactions that result from the exposure of diluted raw exhaust to artificial sunlight take place in eight irradiation chambers. Fluorescent lighting panels composed of blue lamps, black lamps, and sun lamps outside the chamber pass intense ultraviolet radiation through windows of clear teflon FEP fluorocarbon film. Two irradiation chambers are needed to provide the atmosphere for each large animal exposure chamber so that the average irradiation time of the atmosphere is one hour. Normal flow through the irradiation chamber is 0.71 m³/min (25 cfm). Each irradiation chamber has a volume of 19.34 m³ (683 ft³) and they are stacked in pairs to conserve floor space.

5. Animal Exposure Chamber Rooms

There are three animal exposure chamber rooms and each contains eight of the 2.83 m^3 (100 ft^3) volume animal chambers. Each chamber room is individually air conditioned by a 5-ton, self-contained, air-cooled unit located outdoors. It is necessary to maintain controlled temperature in the exposure rooms in order to prevent heat transfer through the walls of the chambers and to avoid stressing the animals when they are removed for examination or chamber cleaning. The animal exposure chambers are constructed of 14-gauge type 304 stainless steel and are cubicle with formed funnels at the top and bottom of each chamber. The normal air circulation rate is 15 volumes per hour or $0.71 \text{ m}^3/\text{min}$ (25 cfm).

6. Monitoring Instrumentation

Sixteen exposure chambers are monitored continuously (approximately once per hour) for carbon monoxide, total hydrocarbons, nitric oxide, nitrogen dioxide, carbon dioxide, and sulfur dioxide. Concentration measurements are collected via an electronic interface between the analyzers and a Hewlett-Packard 3050-B automatic data acquisition system with an attached calculator.

Gas chromatographic measurements of methane, ethane, ethylene, and carbon monoxide are performed periodically. Aldehydes, ammonia, and ozone are also measured occasionally by appropriate methods.

Particulate is measured daily and analyzed for mass, and hydrogen, ammonium, and sulfate ion concentrations. Aerosol size distribution, temperature and relative humidity are also determined daily. The analytical methods for measurement of the atmospheric components in the animal exposure chambers are listed in Table 1.

7. Engine Selection Criteria

In order to meet the needs of program planning under the Clean Air Act Amendments, it was necessary that the engine selected for the study be widely distributed and thereby representative of a typical source of emission. The General Motors Corporation is the largest manufacturer of automotive engines and its Chevrolet model has the greatest distribution of all automobile engines. Furthermore, the Chevrolet 350-CID is the standard engine used as a baseline for emissions development research. Since this engine was thought logically to represent the typical power plant that other sectors of industry and government will be using, it was selected for our studies to provide comparability and relevance.

TABLE 1

ANALYTICAL METHODS FOR MEASUREMENT OF
ATMOSPHERIC COMPONENTS

<u>Component</u>	<u>Primary Method of Analysis</u>
Carbon Monoxide (CO)	Non-Dispersive Infra-Red (NDIR)
Total Hydrocarbons (THC)	Flame-Ionization Detector (FID)
Nitrogen Oxides (NO _x)	
Nitric Oxide (NO)	Chemiluminescence
Nitrogen Dioxide (NO ₂)	Chemiluminescence
Carbon Dioxide (CO ₂)	Non-Dispersive Infra-Red (NDIR)
Sulfur Dioxide (SO ₂)	Flame Photometric Detection (FPD) of Pulsed UV Fluorescence
Specific Hydrocarbons	
Saturated (C ₁ -C ₂)	Gas Chromatography
Olefin (C ₂)	Gas Chromatography
Aldehydes (-CHO)	Colorimetry (MBTH)
Ammonia (NH ₃)	Colorimetry (Phenol-Hypochlorite)
Ozone (O ₃)	Chemiluminescence
Particulate	
Total Mass (M)	Filter Sample Gravimetry
Size	Electrical Precipitation (Mobility)
Hydrogen Ion (H ⁺)	pH Measurement
Ammonium (NH ₄ ⁺)	Colorimetry (Phenol-Hypochlorite)
Sulfate (SO ₄ ²⁻)	Thorin Titration (Optical End-Point)
Chamber Conditions	
Temperature (T, °C)	Thermistor
Humidity (% R.H.)	Wet Bulb-Dry Bulb Relationship

The diesel engine selected is made in Japan by the Nissan Motor Company (makers of Datsun automobiles). It is also the same small engine which the International Harvester Company introduced in 1976 as an option on its new line of Scout II sport-utility vehicles, and on Traveler station wagons and Terra pick-up trucks. For long-term animal exposure studies it is necessary to have automatic cycle control, and this in turn requires an automatic transmission. This feature of the Nissan diesel was a decisive factor in selecting it over the French Peugeot, which comes equipped only with a manual transmission.

8. Gasoline Engine Cycle

The dynamometer driving schedule for the Chevrolet engines consists of a repetitive series of idle, acceleration, cruise, and deceleration modes of fixed time sequences and rates. Table 2 shows this repetitive series of a modified "California" cycle used in present fuel emissions studies.

9. Fuel Selection and Storage

The gasoline selected for use as a standard reference is American Unleaded 91 Octane Test Fuel, Intermediate Grade ("indolene clear"). As a reference, it is important that it be of quite precise and reproducible composition and character. This includes an absence of lead and other additives (except as specifically noted), and should also represent high volume "regular" market gasoline. This gasoline has been used for emissions studies in research and development by industry and other agencies.

There are numerous Federal military and commercial diesel fuel specifications and classifications used by industry. For automobiles, highway trucks, tractors, marine, and off-road equipment, No. 2 diesel is the typical fuel requirement and therefore was selected for the Nissan engine. A fair comparison between the statutory emission levels and those of the engine under test should be made with a fuel that is representative of that in actual commercial use.

There are two underground fuel storage tanks of 2200 gallon capacity, with gasoline stored in one tank and No. 2 diesel fuel in the other. Each tank is equipped with an electric fuel pump to deliver fuel from the main storage supply to a smaller companion tank located outside the building near the engine area. These tanks are provided with a special connection to permit the introduction of fuel additives so that 50 gallon batches can be prepared without contaminating the main tank.

TABLE 2
MODIFIED CALIFORNIA CYCLE OF ENGINE OPERATION

<u>Mode</u>	<u>Speed (M.P.H.)</u>	<u>Time (Seconds)</u>
Idle	0*	20
Acceleration	0 to 30	14
Cruise	30	15
Deceleration	30 to 15	11
Cruise	15	15
Acceleration	15 to 48	29
Peak	48 to 50	1.5
Deceleration	50 to 0	<u>31.5</u>
Total		137

*Drive shaft 100 rpm

B. Automotive Emissions Study

After installation of the physical facilities, a series of animal exposures involving different species were initiated for the purpose of assessing biological effects on the respiratory system. The automotive exhaust generation system consisted of a 1975 Chevrolet engine equipped with the California hardware package, converter, and associated equipment as described under Physical Facilities. The engine was run 16 hours daily and cycled continuously using the 7-mode cycle. The fuel consisted of unleaded 91 octane indolene with thiopene added to produce a high sulfur fuel (0.10% S by weight).

The study consisted of the following experiments which were initiated in CY '76: (1) effects of exposure on pulmonary function in guinea pigs; (2) effects of exposure on pulmonary function in cats; (3) effects of blood gases and pulmonary function in rats; and (4) effects of exposure on susceptibility to respiratory infection.

1. Effects of Exposure on Pulmonary Function in Guinea Pigs

The goal of the experiment was to determine the effects of irradiated and raw catalytically altered exhaust on guinea pig growth rate, cardiac and pulmonary function and respiratory system histology. The design of the investigation included two interrelated parts--acute and chronic exposures.

a. Acute Study - Three groups of guinea pigs were measured in the study. Animals were young and of the same weight as the average six-week-old guinea pig ($400 \pm 50g$). All animals were treated identically with the exception of the exposure to the test gas; one group was exposed to clean air, one to raw catalytically altered auto exhaust and one to irradiated catalytically altered auto exhaust. Exposure time to each test gas was one hour (concentrations were the same as used for the chronic study). Animals were randomly assigned to each group.

Sulfur dioxide (SO_2) has been reported to be a mild respiratory irritant, the inhalation of which results in bronchoconstriction. One-hour exposures have demonstrated an increase in airway resistance in guinea pigs, cats, dogs, and man. Sulfuric acid mist has been shown to have a much greater irritant potency. Both contaminants are found in measurable quantities in the catalytically altered emission atmospheres. We were interested in quantitatively comparing data from animals exposed to emissions with data from those exposed to a known irritant. For this reason, we conducted a parallel study using SO_2 alone.

b. Chronic Study - As in the acute study, three types of test gas (clean air, raw catalytically altered auto exhaust and irradiated catalytically altered auto exhaust) were used. A total of sixty guinea pigs were exposed to each gas type for consecutive periods of six and twelve

weeks (16 hr/day, 7 days/week) starting the first week of life. Thirty animals from each group were exposed for each time period. The sixty guinea pigs of each group were divided equally into three exposure chambers (20/chamber) where they lived and were exposed to the test gas for 16 hours each day; there were three different chambers for each group. Exhaust concentration for each group was maintained at a constant dilution and characterized throughout the time of the experiment. Animals were staged into and out of the exposure periods. The schedule was arranged so that baby animals were randomly selected from litters each week, and distributed between the three test atmospheres. Each animal was numbered, half were tested after six weeks of exposure and half after twelve weeks of exposure.

c. Methods and Equipment - Physiological methods for evaluation of pulmonary function of guinea pigs have been developed and described by Amdur and Mead. Three simultaneously recorded measurements are necessary--intraplural pressure, tidal volume, and air flow rates into and out of the lungs. Certain modifications of their techniques were made by our laboratory to eliminate the need for anesthesia and surgery on the day of measurement. A body plethysmograph and single animal exposure chamber was designed and constructed that allowed for physiological measurement of unanesthetized guinea pigs during exposure to test atmospheres. Pressure, flow, and concentration of each test atmosphere was controlled in this chamber. A Statham P23Db pressure transducer was used for intraplural pressure measurements. The transducer was in direct communication with a saline-filled silastic catheter inserted into the guinea pig intraplural space. A Statham PM5 differential pressure transducer, connected to the body plethysmograph was used to measure tidal volume. Flow was measured by electrical differentiation of the tidal volume signal with respect to time. Pulmonary flow resistances were computed at maximal flow rates and expressed in $\text{cmH}_2\text{O}/\text{ml}/\text{sec}$. Dynamic compliance was obtained at maximum tidal volume and expressed as $\text{ml}/\text{cmH}_2\text{O}$.

Both phases of the experiment (acute and chronic) started on November 15, 1976. Guinea pigs were placed in exposure chambers for the chronic study and measurements on acute study animals were initiated. Infant guinea pigs were continually placed in the chambers until December 29, 1976. Chronic exposure of guinea pigs was scheduled for completion March 25, 1977, and physiological measurement of all animals, acute as well as chronic, will be implemented by June 1977; a final report on this work is anticipated by October 1977.

2. Effects of Exposure on Pulmonary Function in Cats

This experiment was designed to determine the effects on inhalation exposure to catalytically treated exhaust upon pulmonary function and histopathology. Cats were used as experimental animals because they are a larger species and this facilitates the use of a wider range of pulmonary function tests. Also, comparison of the pulmonary effects in several species would aid in the extrapolation to humans.

The cats were divided into two groups with one group exposed to exhaust and the other group to clear air. The animals were exposed for 16 hours per day for 90 days. After the completion of the exposure period, the cats were removed individually from the exposure chambers, anesthetized, and prepared for pulmonary function measurements. Pulmonary function measurements with the exception of helium washout were conducted with the aid of an animal plethysmograph. Following anesthesia and tracheotomy, the cat was placed on its back in the plethysmograph. The door was sealed, the tracheal cannula connected to the pneumotachometer, and the intraplural catheter connected to the pressure transducer. Intraplural pressure, respiratory volume and flow were recorded. The cat was then automatically respired by cyclic pressure changes with a range of ± 20 cmH₂O pressure at rates of 40, 70, 110, 140, and 160 cycles/minute. Dynamic compliance and resistance were calculated. Expiratory flow volume measurements were then determined by suddenly decreasing the pressure in the plethysmograph to -60 cmH₂O pressure followed immediately by a sudden increase in pressure to 60 cmH₂O. At least four maximal expirations were recorded with two plotted as volume and flow versus time and two plotted as flow versus volume. The cat was then removed from the plethysmograph and connected to the Howard respiration pump. Stroke volume was set at 15% of vital capacity. The cat was hyperventilated for several minutes to inhibit respiratory efforts. Ten percent helium was then inspired until the expired helium concentration was stable. The animal was then switched to room air. Helium concentration was monitored and the number of breaths required to reduce the expired He to 1% of the original concentration was recorded. The measurements were repeated at 25, 50, 75, and 100 breaths per minute. After completion of the pulmonary function measurements, the cats were sacrificed and tissues taken for histopathology.

Measurements will be completed in April 1977, and a report prepared during CY '77.

3. Effects of Exposure on Arterial Blood Gases and Pulmonary Function in Rats

Groups of 20 rats each were exposed 16 hours per day for 45 or 90 days to the automotive catalytically treated exhaust. Parameters measured include body weight, food intake, lung weights, static lung compliance, functional residual capacity, hematocrit, hemoglobin, P_{O_2} , and P_{CO_2} .

Following completion of exposure, the rats were removed individually from the chamber, briefly anesthetized and catheter implanted in the caudal artery. After regaining consciousness, an arterial blood sample was collected. The rat was then placed in a small chamber with the arterial catheter and a rectal temperature probe ducted to the exterior. The chamber was flushed with 100% oxygen and a blood sample collected after 10 minutes. The chamber was then flushed with 9% oxygen for an additional

10 minutes and a final arterial blood sample collected. Analysis of arterial PO_2 and PCO_2 were carried out on all three blood samples. Hematocrit and hemoglobin content were measured on the first sample. After completion of blood collection, the rats were reanesthetized and a cannula placed in the trachea. Functional residual capacity (FRC) was measured by injecting a known volume of gas containing 10% helium into the lungs at the end of a normal expiration. An equal volume was withdrawn 10 second later and the helium content analyzed and the functional residual capacity calculated. After measurement of FRC, the rat was administered pure oxygen for 5 minutes to flush out all nitrogen. The animal was then asphyxiated, the chest wall incised and the aorta and vena cava severed. The lungs were filled with air to a pressure of 30 cm H_2O . Volume was recorded at each pressure with the final recording at ambient pressure. Deflation curves of transpulmonary pressure plotted against percent of total lung volume were made for each animal. After compliance was measured, the lungs were removed, weighed, and fixed for histopathology. Analysis of data from these animals will be completed in CY '77.

4. Effects of Exposure on Susceptibility to Respiratory Infection

As part of the multidisciplinary effort to evaluate the biological effects of inhalation exposure to automotive catalytically treated exhaust, a series of experiments were performed in mice to assess the effects on susceptibility to infection by pathogenic microbes. The basic experimental design used in the infectivity studies consisted of: (1) a control group which was exposed to clean air, the removed and exposed in a separate chamber to an atmosphere containing suspended aerosol of pathogenic bacterial broth culture (challenge) followed by observation for morbidity and mortality; and (2) the experimental group was exposed to diluted exhaust atmosphere followed by exposure to the infections aerosol challenge, followed by observation for morbidity and mortality. Experimental group data (mortality and body weight) were then compared with control data to detect the relative difference reflecting exhaust-exposure effect. The experimental hypothesis asserts that exhaust exposure will enhance susceptibility to lethal infection, so that mortality in the exposed group will exceed the control group. Principal variations within the basic design framework included: (1) type of exhaust; (2) duration of test exposure; (3) single versus multiple intermittent infectious aerosol exposure; and (4) age of animal.

Preliminary results indicate a significant enhancement of susceptibility to lethal infection following exposure to catalytic auto exhaust. There was a significantly greater enhancement effect in mice exposed to irradiated exhaust. Early indications suggest that the greater irradiated exhaust effect may be attributable, at least in part, to a higher concentration of nitrogen dioxide. Further interpretative efforts in relation to exhaust components must await finalization of aerometry data. There was

no clear evidence of a dose-effect relationship with respect to duration of exposure. The effects of enhanced susceptibility to infection was, in most respects, as great, or nearly so, in the acute as in the more prolonged experiments. Analysis of the data will be completed in CY '77.

C. Diesel Emissions Study

Installation of much of the hardware for the diesel study was completed in CY '76 as described in Physical Facilities. Protocols have been developed for the operation and measurement of the emission atmospheres. After completion of the automotive emissions study in CY '77, the diesel engine will be put into operation and the development of the engine cycle will be tested along with characterization of the emissions in various locations within the system. Following completion of engine testing and emissions characterization, biological exposures will be initiated.

D. Ultrafine Sulfuric Acid and Metal Sulfates

The current status of investigations of the biological effects of exposure to H_2SO_4 and other metal sulfates are described below. The work was conducted both in-house and extramurally. The exposures to sulfuric acid did not include the ultrafine range because development of the generation system has not been completed.

1. Pulmonary Effects of Inhaled Aluminum Sulfate and Sulfuric Acid

Aluminum sulfate and sulfuric acid were selected for use in a study designed to establish whether toxicity of sulfates is due to the sulfate anion ($SO_4^{=}$) or to the associated cation metal or proton. The aluminum salt was chosen because (a) the base material of certain converters is alumina, (b) the presence of this metal in airborne particles is almost inevitably due to its abundance in the earth's crust, (c) the burning of coal may increase atmospheric levels of aluminum, and (c) it is considered to be relatively non-toxic.

Pregnant Sprague-Dawley rats, with a mean body weight of 200 g., were divided into three groups and placed in inhalation chambers. The control group received clean air (C); the aluminum-sulfate-exposed group (AL) received $2.4 \pm 1.07 \text{ mg/m}^3 \text{ Al}_2(\text{SO}_4)_3$, the mean particle size was $1.6 \pm 0.25 \mu$; the sulfuric acid-exposed group (SA) received $4.05 \pm 1.63 \text{ mg/m}^3$, for the first 2 weeks, thereafter the concentration was adjusted to $4.80 \pm 0.51 \text{ mg/m}^3$, with mean particle size of $2.75 \pm 1.25 \mu$. The lengths of exposure for the dams (D) were 67, 66, and 65 days for D-C, D-AL, and D-SA groups, respectively. At the end of exposure, 10 dams and 10 pups, chosen at random, were killed and studied for pulmonary effects.

The parameters monitored in this experiment were primarily those involving the alveolar macrophage, population and morphology, the level of lysozyme spilled in the alveolar space and the permeability of the lung wall as measured by the leakage of i.v.-injected albumin- ^{131}I into the alveolar fluids. The selection of these parameters is based on the hypothesis that injury to macrophages by the inhaled toxicant with consequent spillage of lysosomal enzymes in the alveolar fluid will initiate an inflammatory process and produce an alteration of the permeability of the alveolar wall. We also measured serum trypsin inhibitory capacity, serum proteins and enzymes such as GOT, LDH, and GPT.

The results indicated a significant increase in the number of alveolar macrophages, as collected by lung lavage, was observed in both AL and SA groups; however, the morphology of the macrophages from AL group presented abnormalities such as swelling and granulation while the macrophages from SA group appeared normal. Lysozyme activity in the cell-free lavage was shown by the radioactivity of the lung lavage was increased 5-fold in the D-AL group but remained normal in the DSA group. When ^{131}I counts in the lavage were plotted against lysozyme activity, we obtained a high correlation coefficient ($r \pm 0.904$, $n = 29$) with less than 10% relative standard deviation of the slope.

We also obtained the electrophoretic patterns of serum proteins in pups. The data showed significant alteration in albumin, α_1 , α_2 , β and γ -globulins. Serum albumin levels were reduced below control values by both sulfuric acid and aluminum sulfate inhalation. Aluminum caused a reduction below controls in levels of α_1 -globulin, α_2 -globulin and γ -globulin, while sulfuric acid caused a reduction in the α_2 -globulin level but raised the γ -globulin level considerably.

These data have shown that: (a) the irritating effects of sulfuric acid and aluminum sulfate on lungs were reflected in the number of the alveolar macrophages collected in the lung lavage; (b) the morphological changes of the collected macrophages in the aluminum sulfate-exposed animals, which did not occur in the sulfuric acid-exposed groups, suggest that the cation is responsible for this effect; (c) the spillage of lysosomal enzymes, as shown by lysozyme activity, may be due to the deleterious effect of Al^{3+} on the macrophage and other lung cells; (d) the change in the lung wall permeability, as shown by albumin- ^{131}I counts in the lung lavage, was related to the high concentration of lysozyme in the cell-free lung fluid; and (e) sulfate by itself, in the form of sulfuric acid and at the concentration used, did not seem to produce pronounced effects on the lung as did aluminum sulfate, and serum protein profiles were disturbed by both sulfuric acid and aluminum sulfate, but in different ways to different degrees.

From these results, it seems to follow that aluminum cation is more irritating to rat lungs than is either the hydrogen ion or sulfate anion (SA) and that much more attention and concern should be given to the health effects of cations in the environment than to the small amount of sulfuric acid produced by the catalytic converter.

2. Effects of Exposure to Sulfuric Acid and Platinum Sulfate Aerosols on Susceptibility to Respiratory Infection from Inhaled Bacterial Aerosol

Sulfuric acid and platinum sulfate aerosols were tested for their relative toxicity with respect to influencing susceptibility to inhaled pathogenic bacteria. Female mice aged 3-4 weeks were exposed to groups of 10. Each experiment constituted a 2 x 2 factorial design and included exposure to: (a) neither test material nor infectious challenge (controls); (b) infectious aerosol challenge only; (c) test material aerosol only; or (d) test material aerosol plus infectious aerosol challenge.

Two concentrations of sulfuric acid aerosol (242 and 26.7 mg $\text{H}_2\text{SO}_4/\text{m}^3$, respectively; particle size estimated at 0.82 and 0.48 μm MMAD, respectively) and one of platinum sulfate (13.1 mg Pt (SO_4) $_2 \cdot 4\text{H}_2\text{O}/\text{m}^3$ or 5.6 mg Pt/ m^3 ; particle size estimated at 0.4-0.5 μm MMAD) were tested using an exposure duration of 3.62 hours. Exposures were followed by infectious challenge. The mice were observed for mortality, body weight change, and overt toxicity or illness for at least 15 days following challenge.

Lethal response to infective aerosol exposure was significantly ($p < 0.05$) in the mice exposed to platinum sulfate plus infective aerosol relative to the corresponding infection-only group. Apart from apparent irritant responses during exposure, no gross signs of overtly toxic effects were obvious in mice exposed just to pollutant aerosols.

These results indicate that inhalation of the high, but not the low, level of sulfuric acid aerosol, and of the platinum sulfate aerosol at a relatively low level, resulted in enhanced susceptibility (impaired resistance) to disease induced by inhaled pathogens, and further, that the metallic sulfate aerosol was comparatively much more toxic in this respect than the sulfuric acid on a mass dose basis. These findings are consistent with other work indicating greater toxicity of certain metallic sulfates than of sulfuric acid.

3. Effects of Exposure of Rats to Sulfuric Acid, Sulfur Dioxide, or Aluminum Sulfate

Rats were exposed continuously for periods ranging from 6 to 14 weeks to sulfuric acid, sulfur dioxide or aluminum sulfate. Pulmonary function studies indicated that the aluminum sulfate was most detrimental. Exposure to aluminum sulfate at a concentration of 2.04 mg/ m^3 and having a mass median aerodynamic diameter (MMAD) of 2.0 μm resulted in increased static deflation volumes in juvenile rats but exposure decreased

the static deflation volume in the guinea pig. Exposure to either sulfuric acid (4.05 mg/m^3 , MMAD of $0.5 \mu\text{m}$) or aluminum sulfate caused an increased pulmonary resistance and respiratory rate in adult rats. Spontaneous locomotor activity during exposure and treadmill performance for up to 40 days post-exposure were significantly decreased by exposure to aluminum sulfate having a MMAD of $1.4 \mu\text{m}$ and a concentration of 2.59 mg/m^3 .

4. The Direct Measurement of Sulfuric Acid Mist in the Lung

The object of this study was to directly measure the depth of penetration of sulfuric acid particles in the lungs of beagle dogs. This was to be carried out by implanting a small catheter containing a filter in an airway no larger than 1-2 mm in diameter. The sulfuric acid particles would be collected on the filter and visualized directly with the aid on an electron microscope.

Numerous delays and difficulties arose from attempting to collect and characterize sulfuric acid particles on the filter. The contract effective date was October 15, 1975, with a six-month performance period. This was eventually increased to fourteen months with a final date of December 15, 1976. The investigators were finally successful in generating sulfuric acid mist of the correct particle size, collecting the mist on a filter and counting the particles. When an attempt was made to use this system in the dog, however, no sulfuric acid particles could be collected. This was true even if the tube and filter were placed at the upper end of the trachea near the source of the mist.

At this point, time had run out and funds were depleted. Although possible reasons for failure were discussed, an adequate explanation was not achieved. A decision was made not to fund the project further since we had no assurance that it would be carried out successfully.

E. Manganese Oxide Studies

In October 1976, it was decided to reprogram some of the efforts in the Catalyst Research Program to address the problem of manganese toxicity following inhalation exposure. The lung has been incriminated as the major portal of entry in case of Mn intoxication in man. However, there is evidence that much of the inhaled Mn is transferred by the mucociliary ladder to the gastrointestinal tract, from which it is either absorbed or eliminated. Mena, et al. conducted a series of ^{54}Mn exposures in humans using oral and inhalation routes. From these exposures, the investigators concluded that the gastrointestinal tract was the portal of entry for most of the inhaled Mn. This observation is in conflict somewhat with those of other investigators. In the case of lead, it has been estimated that 30 to 50% of inspired Pb is absorbed by the lungs and 10% swallowed Pb by the gastrointestinal tract.

Preliminary experiments in this laboratory have indicated a marked difference in the absorption of $^{54}\text{MnSO}_4$ when administered orally and intratracheally. However, intratracheal administration has a number of disadvantages which may affect retention.

Current experiments are designed to investigate the retention, tissue distribution, and excretion following acute inhalation exposure to $^{54}\text{MnSO}_4$ and $^{54}\text{Mn}_2\text{O}_3$ aerosols. Comparisons will be made as to the effect of chemical form on the retention of manganese.

IV. PROBLEM AREAS

Conducting inhalation research is expensive, especially if the tasks involve the investigation of biological effects of exposure to whole emissions from automotive engines. The Health Effects Research Laboratory-Cincinnati has the physical facilities for inhalation exposure of laboratory animals to total automotive and/or diesel emissions and to single pollutants. There are 25 large exposure chambers associated with the automotive exhaust generation system and 46 exposure chambers available for single pollutant studies. The current funding is not sufficiently large to permit full utilization of the exposure chamber space. The current budget is barely adequate to meet salary and operation costs. In-house funds per man-year were \$27.18K which is certainly minimal for this type of work. Existing contracts were funded from funds available in past years and there are no funds available for renewal of extramural support.

Other problems involve technical aspects of individual studies. In the manganese studies, the determination of the appropriate chemical form of Mn for use in the inhalation studies is of concern. Based on data supplied primarily by industry, it has been assumed that the combustion product of methylcyclopentadienyl manganese tricarbonyl was Mn_3O_4 . However, recent data has indicated that Mn_3O_4 was also found in dilution tunnel sweepings. Further, in a memorandum from Mr. Thomas Murphy, Deputy Assistant Administrator for Air, Land, and Water Use, EPA, it is stated that the probable species is Mn_2O_3 (actually $\text{MnO}(\text{OH})$). The oxidation state of Mn is important to determine because some investigators have postulated that the lower oxidative states are more toxic than higher ones. This has often been reported but not experimentally documented. Indeed, dose-response relationships have not been done to determine if the toxicity of manganese is influenced by its physical form. Initiation of the ultrafine sulfuric acid study awaits the arrival of a generation system being developed through a contract by EPA-Research Triangle Park. However, HERL-Cincinnati, through modification of an existing generation system, possibly has an ultrafine sulfuric acid generation system that, according to preliminary measurements, is producing an acid aerosol of about $0.02 \mu\text{m mmd}$ over the range of $10\text{--}100 \mu\text{g}/\text{m}^3$ in a test chamber. Current work involves confirmation of concentration levels.

V. PLANS FOR FUTURE RESEARCH

Future research plans can be broken down into four major areas: (1) completion of current automotive catalytic emissions study; (2) studies on the biological effects of exposure to diesel emissions; (3) biological effects of ultrafine sulfuric acid and metallic sulfates; and (4) toxicity of airborne manganese oxides associated with the combustion of methylcyclopentadienyl manganese tricarbonyl (MMT).

A. Automotive Catalytic Emissions Study

The current exposures will be completed in April 1977. Data analysis and preparation of reports will be finalized in CY '77.

B. Automotive Diesel Emissions Study

The Center Hill Road facilities to be used for the diesel exhaust study are the same as have been used for the previous study of catalytic converter exhaust emissions. The most notable change will be the substitution of an automotive-type diesel engine. Future plans for engineering and aerometry in the diesel study during CY '77 require cycle testing and characterization of the entire exhaust generation and animal exposure chamber system using several steady state speeds before attempting to measure the average emissions under automatic cycle control. Since both the magnitude and nature of the losses will vary with engine speed and dilution factor, the optimum operating conditions will be determined before the animal exposures are started. Material balances for carbon and sulfur will require both tailpipe- and dilute-particulate sampling at steady state speeds.

The guideline for maximum deterioration allowable in engine emissions will be based on Federal Register vehicle certification procedures. Published emissions deterioration factors allowable over 50,000 miles can be applied as a "not to exceed" limit. In the chronic exposure, our operation will be 16-20 hours each day of the week at approximately 20 mph average cycle speed, therefore, mileage accumulation could exceed 100,000 miles per year. Since this approaches half the life of the diesel engine, a spare engine will be obtained if the feasibility of using the Nissan engine is found to be acceptable for biological studies.

Aerometry procedures and instrumentation will include the best available approaches that will satisfy research requirements. A quality assurance plan has been developed and quality control procedures have been formalized. The aerometry staff will work closely with RTP laboratories to insure that all quality measurements are accurate as the state-of-the-art permits. In addition to the in-house effort, there will be independent audits of the aerometry measurements conducted by an outside contractor.

During CY '77 a protocol for the first biological study that will be initiated in the assessment of toxicity following exposure to diesel emissions will be prepared and the actual exposures will begin in November 1977. The primary objective of the first diesel emission study is to gather sufficient information for: (a) preliminary toxicological assessment of the atmospheres; and (b) development of a second more specialized protocol. It should be realized that this experiment is the first attempt at exposing animals to diesel exhaust at HERL. There is very little information in the literature to serve as a guide for anticipation of possible biological effects. This is particularly true for diesel particulate. Data on the composition of diesel emissions suggest a strong possibility of biological effects, considering the content of irritant and aromatic hydrocarbons and the respirable particulate. Major emphasis of the research approach in this protocol will be in evaluating the major target organ--the lungs. The laboratory has extensive experience in assessing lung changes by pulmonary function, biochemical and histopathological approaches. Thus, as a starting point, this protocol will assess the effects of inhalation upon the same biological parameters as measured in the automotive catalytic emissions study. This approach will permit comparisons with previous automotive exhaust studies.

The parameters to be measured in the first diesel exposure study include: (1) pulmonary function in rats, guinea pigs, and cats; (2) susceptibility to infection in mice; (3) histopathology and clinical chemistry in rats; (4) biochemical alterations in the lungs using rats and guinea pigs; and (5) spontaneous locomotor activity in rats. The duration of exposure will be 20 hours a day for 30 days.

Based on the data obtained from this exposure to diesel exhaust, a more specialized protocol will be developed for the second study. This will include the use of extramural contracts supported by carry-over funds to provide the capability in (1) mutagenicity-carcinogenicity testing of diesel exhaust condensate, (2) measurement of collagen precursors in the lung, (3) teratogenicity testing, and (4) a three generation study.

C. Ultrafine Sulfuric Acid and Metallic Sulfates

The current studies on sulfuric acid and metal sulfates will continue with major emphasis being shifted to exposures to ultrafine acid as generation equipment becomes available. These experiments include exposures of guinea pigs to ultrafine sulfuric acid, short and intermediate term effects of exposure of rats to ultrafine sulfuric acid alone or with ozone, biochemical alterations in rats following exposure, and effects on susceptibility to infection.

1. Guinea Pig Exposures

Unanesthetized guinea pigs will be exposed for one hour to fine particulate ($0.01\mu - 0.1\mu$) sulfuric acid at a concentration of approximately $100 \mu\text{g}/\text{m}^3$. Pulmonary function measurements will be recorded from each animal during exposure. Measurements include airway resistance, lung compliance, breathing rate, tidal volume, minute volume, and ECG. To obtain signals for these measurements, each animal is fitted with a saline-filled intraplural catheter and placed in a body plethysmograph. Three groups of guinea pigs will be tested: (1) Group I animals will serve as controls; (2) Group II animals will be exposed to H_2SO_4 ; and (3) Group III will consist of sensitized animals exposed to the same test atmosphere as Group II. Temperature and humidity of test atmospheres will be controlled.

2. Exposure of Rats to Ultrafine Sulfuric Acid and Ozone

Theoretical considerations suggest that the maximum concentration of ultrafine sulfuric acid attainable is approximately $100 \mu\text{g}/\text{m}^3$. While this concentration may produce no detectable toxicological effects alone, its activity may well be enhanced by presence of other pollutants.

The study using rats is designed to measure the toxicological effects of an ultrafine sulfuric acid alone and in combination with ozone. The emphasis will be upon functional and pathological alteration of the lung. A wide range of concentrations of pollutants will be used initially. Specific questions to be considered include: (a) the toxicological properties of ultrafine sulfuric acid mist, (b) possible enhancement of the toxicological properties of ozone including influence on threshold levels as well as mortality, and (c) the influence of low levels of ozone upon detection limits for biological changes due to ultrafine sulfuric acid.

Groups of ten to twenty rats each will be exposed to the maximum level of sulfuric acid attainable and sacrificed after exposure periods, ranging from 1 to 28 days. Separate groups will be exposed to ozone concentrations ranging from 0.2 to 4 ppm alone and in combination with sulfuric acid for similar periods of time. The group size may be adjusted depending upon within-group variance of the parameters being measured. All exposures will be eight hours per day, five days per week. Body weight, food consumption, general condition, and mortality will be monitored. Measurements will include arterial blood Po_2 , Pco_2 , pH, standard bicarbonate, hemoglobin, hematocrit, white cell counts, differential counts, total lung capacity, vital capacity, residual volume, functional residual capacity, static pressure volume curves and histopathological changes.

3. Biochemical Alterations Following Exposure

Biochemical alterations will be assessed in animals following acute and chronic exposures to MnSO_4 , $\text{Al}_2(\text{SO}_4)_3$, and ultrafine H_2SO_4 . The parameters that will be studied in these exposures are primarily those

involving the alveolar macrophage (population and morphology), the level of lysozyme spilled in the alveolar space, and the permeability of the lung wall as measured by the leakage of i.v.-injected albumin - ^{131}I into the alveolar fluids. Additional work is planned to study the effects of these aerosols on the connective tissue of the lung. Lung protein synthesis (collagen synthesis) will be investigated.

4. Ultrafine Sulfuric Acid Aerosol Infectivity Study

Assess toxicity of ultrafine sulfuric acid with respect to effect on susceptibility to respiratory infection. Mice will be exposed for varied periods to ultrafine H_2SO_4 aerosol and to a superimposed challenge with aerosol containing pathogenic bacteria. Comparative infective response in test-versus-control subjects will discern induction of impaired resistance to infection.

D. Manganese Oxide Studies

Plans for the Mn investigations are designed to examine changes in the lungs and CNS after exposure. The effects on the lungs will be assessed using pulmonary function techniques, the infectivity model, biochemical assays, and histopathological examination. Any neurological impairment will be determined through behavioral tests and measurement of biochemical alterations in neurotransmitters.

1. Effects of Manganese Oxide on Pulmonary Function and Other Clinical Parameters

Disease-free cats will be exposed to Mn_2O_3 continuously for period of six months. Groups of 11 cats each will be exposed to clean air, Mn_2O_3 25 $\mu\text{g}/\text{m}^3$ or Mn_2O_3 $\mu\text{g}/\text{m}^3$.

Measurements will include body weights and food intake. At the end of exposure, the cats will be anesthetized and a series of pulmonary function measurements made. These will include maximum expiratory flow-volume curves, dynamic compliance, frequency dependence of compliance, helium washout, total lung capacity, vital capacity, residual volume, etc.

Blood samples will be collected for hematocrit, red and white cell counts, differential counts, pH, and standard bicarbonate. The lungs will then be infused with 10% buffered formalin at 30 cmH_2O pressure and examined for pathology.

Biochemical and clinical chemistry measurements will also be made on these animals, including Mn concentrations in the various tissues.

2. Effects of Manganese Oxide on Neurophysiological and Behavioral Parameters

Adult rats will be exposed to manganese oxide via inhalation at several different levels. General toxicity tests, as well as specific tests, assessing neurophysiological function and behavior will be performed (spontaneous activity, electroencephalographic changes, visual-evoked response). After completion of this task, neonatal exposures will begin. Similar tests will be performed as above; however, an attempt will be made to assess the effect of these exposures on the development of the central nervous system.

3. Manganese Oxide Aerosol Infectivity Study

Effects of exposure to airborne particulate manganese oxide on susceptibility to respiratory infection will be determined. Mice will be exposed to manganese oxide aerosol atmospheres at varied levels and for brief to moderate durations, and to a superimposed challenge with pathogenic bacteria. Infective response (morbidity, mortality) between controls and exposed animals will be compared to determine if enhancement of susceptibility has occurred.

VI. CONCLUSIONS

The Catalyst Research Program at the Health Effects Research Laboratory-Cincinnati has been designed to provide EPA with biological data on the toxicologic effects of mobile emissions, emission control devices and fuel additives. The major effort during CY '76 was the construction of a new mobile emissions animal exposure facility at the EPA Center Hill Road laboratory and the installation of animal exposure chamber at the Environmental Research Center. The mobile emissions animal exposure facility was completed in the Fall and animal exposures to automotive catalytic emissions were initiated. These studies will not terminate until April 1977, so no conclusions can be reached on the biological effects of exposure.

Exposure of mice to catalytic auto exhaust resulted in enhancement of susceptibility to lethal infection. There was significantly greater enhancement of effect in mice exposed to irradiated exhaust than in those exposed to nonirradiated exhaust.

Inhalation exposure of rats to aluminum sulfate and sulfuric acid indicated that the aluminum cation was more irritating to the lungs than is either the hydrogen ion or sulfate anion.

In rats and guinea pigs exposed to sulfuric acid, sulfur dioxide or aluminum sulfate, pulmonary function indicated that aluminum sulfate was the most detrimental. Exposure to either sulfuric acid or aluminum sulfate caused increased pulmonary resistance and respiratory rate in adult rats.

Spontaneous locomotor activity during exposure and treadmill performance for up to 40 days post-exposure were significantly decreased by exposure to aluminum sulfate.

Inhalation exposure of mice to a high concentration ($242 \text{ mg H}_2\text{SO}_4/\text{m}^3$) of sulfuric acid for 3.6 hours resulted in increased susceptibility to infection. Inhalation exposure of mice to a low concentration ($13.1 \text{ mg Pt}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) of platinum sulfate for 3.1 hours resulted in increased susceptibility to infection.

The CRP for CY '77 consists of completion of automotive catalytic emissions study and initiation of research on the biological effects of exposure to: (1) diesel emissions; (2) ultrafine sulfuric acid; and (3) manganese oxides.

APPENDIX D

THIRD ANNUAL CATALYST RESEARCH PROGRAM REPORT

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I. BACKGROUND AND INTRODUCTION

The Catalyst Research Program (CRP) was initiated in 1974 by the Environmental Protection Agency (EPA) Administrator Russell Train, concurrent with the Agency's decision in November 1973, to permit the use of the noble-metal oxidation catalyst as an emission control device on 1975 model-year passenger vehicles. The program, which resides in the Office of Health and Ecological Effects, encompasses a multi-disciplinary research effort to assess the health and environmental impact of catalytic control technology for mobile emission sources. The program office provides overall guidance and coordination of the projects within the Cincinnati and Research Triangle Park Health Effects Research Laboratories (HERL's), the Environmental Monitoring and Support Laboratory (EMSL), and the Environmental Sciences Research Laboratory (ESRL) at the Research Triangle Park. The responsibilities of HERL/RTP include administrative support and the preparation of reports, position papers, testimony, and other program documents for various Agency needs.

A substantial portion of research activities, as well as the program's coordination function, also resides in HERL. In its affiliation with the CRP, HERL has been involved mainly in sulfate studies (focusing primarily on sulfuric acid), studies of trace metals associated with catalyst-equipped vehicles (focusing mainly on platinum compounds), and a study of emissions from consumer-owned national standard catalyst-equipped vehicles.

II. OVERVIEW

The activities of HERL/RTP in 1976 under the auspices of the Catalyst Research Program may be categorized in four major areas of research: animal studies on sulfuric acid, animal studies on metals, human studies on sulfuric acid, and characterization of in-use vehicles. There was, in addition, one project managed by HERL/RTP on effects of sulfuric acid on vegetation.

A. Animal Studies on Sulfuric Acid

Studies of the effects of inhalation exposure to sulfuric acid involved several parameters. The first set of experiments related to effects on the immune systems of rabbits. Results of a single 2-hour exposure to 1 mg/m³ concentration of sulfuric acid with a particle size of 0.3 μ m-0.5 μ m showed no significant alterations in cell-mediated immune function of circulating lymphocytes. An exposure of 4 hours per day for 2 days showed a marginally significant ($p < 0.1$) alteration. Effects on the

humoral immune system were examined using white mice exposed for 2 hours to $1 \mu\text{g}/\text{m}^3$ sulfuric acid prior to intraperitoneal (IP) immunization with sheep erythrocytes. The acid mist at this level showed no statistically significant effect.

Hematological changes were also observed during the immunological investigation. A decrease of hematocrit that occurred in rabbits following the single 2-hour exposure was found to be statistically significant ($p < 0.05$). Also, though no significant effect on the number of leucocytes per cubic centimeter (cc) was found as a result of exposure, an increase in the number and percent of polymorphonuclear leucocytes and a decrease in the number and percent of lymphocytes were found in both sulfuric acid-exposed rabbits and the control group. These effects were more pronounced in the exposed rabbits ($p < 0.05$). This may indicate that there was some type of nonspecific stress which was enhanced by the sulfuric acid.

The possibility of exposure to other pollutants occurring at or near the same time as exposure to sulfuric acid led to an experiment in which the mouse infectivity model was employed to assess effects of sequential exposure to sulfuric acid and ozone. In this test system mice are exposed to a pollutant or clean air (controls) before receiving an aerosol of viable bacteria. An enhancement of mortality from the ensuing pneumonia is indicative of increased susceptibility to infectious respiratory disease. Results of these experiments showed that when exposure to first ozone ($.196 \text{ mg}/\text{m}^3 \times 3 \text{ hr}$) and then sulfuric acid ($1 \text{ mg}/\text{m}^3 \times 2 \text{ hr}$) preceded the challenge by the infectious agent, the observed mortality was equal to the additive effect of two pollutants. This was not the case when the sequence was reversed and the animals were exposed to sulfuric acid, then ozone, and then the infectious agent. Further work with these sequential exposures (O_3 , then H_2SO_4) involved measurement of tracheal ciliary beating frequency, an indicator of upper respiratory clearance functioning. A two-hour sulfuric acid exposure, at $1 \text{ mg}/\text{m}^3$, but not at $0.5 \text{ mg}/\text{m}^3$, caused a statistically significant depression in ciliary activity. When a three-hour acid aerosol ($1 \text{ mg}/\text{m}^3$) was administered, the observed decrease in ciliary beating frequency was that which would be expected from sulfuric acid alone.

B. Animal Studies on Metals

1. Manganese

In order to clarify the relationship between manganese inhalation and infectious respiratory disease, inhalation studies of acute exposure of respirable manganese aerosols were performed in conjunction with a laboratory-induced streptococcal infection. Following a 2-hour inhalation of manganese (Mn) at $\geq 2.0 \text{ mg Mn}/\text{m}^3$ for the insoluble manganous-manganic oxide and $\geq 3.2 \text{ mg Mn}/\text{m}^3$ for soluble manganese chloride aerosols,

a statistically significant enhancement in respiratory infections was observed. There was also delayed clearance and an increase in the growth of inhaled streptococci in the exposed animals.

2. Platinum

Several studies relating to platinum and palladium are nearing completion, and final reports are expected in 1977-78. Major findings of the current research include the following:

a. Platinum alone or in the complexed state will not induce any type of allergy. Palladium alone is without effect, but when complexed with albumin will induce a delayed allergy which can be transferred via spleen cells.

b. A study underway at Stanford is investigating the effect of platinum or palladium sulfate on leucocyte metabolism and chromosomal aberrations; alteration of platelet metabolism, immunological response, and PMN neutrophil phagocytosis; and enzyme changes in the liver, kidney, and heart. Preliminary results reveal that platinum sulfate has little or no effect on the selected parameters except as a severe eye irritant.

c. Preliminary results of a study at the State University of New York at Buffalo on the effects of platinum sulfate in the central nervous system suggest that the metal has a moderately depressive effect on behavior.

d. Work at Lawrence Livermore Laboratory has established that platinum (as platinum sulfate or potassium hexachloroplatinate) can be methylated, under laboratory conditions, by reaction with methyl B_{12} .

The other studies on platinum, all of which are nearing completion, have not yet begun to report results.

C. Human Studies on Sulfuric Acid

Early in 1977, the Catalyst Research Program is planning to initiate a study of human exposure to sulfuric acid. The study will seek to build a data base on the effects of sulfuric acid aerosol in a concentration range of 50 to 200 $\mu\text{g}/\text{m}^3$ with a mass median diameter particle size range of 0.05 to 0.5 μm ; these ranges are intended to reflect the increased sulfuric acid burden expected from the increased use of the catalytic converter. The study will be performed on healthy male volunteers, and the test parameters will primarily be measurements of pulmonary function.

D. Vegetation Studies on Sulfuric Acid

When vegetation was exposed to submicrometer sulfuric acid aerosol in a greenhouse facility at the University of Minnesota, hybrid poplar, pinto bean, and soybean showed marginal and tip necrosis, symptoms similar to those caused by fluoride- and chloride-induced injury on broadleaved plants.

E. Characterization of In-Use Vehicles

In cooperation with the New York State Department of Environmental Conservation, the EPA is conducting a research project to measure the sulfate, particulate, and regulated emissions for a group of 49 in-use catalyst vehicles. Each car is subjected to a sequence of test-driving modes: a 1975 Federal Test Procedure; a 1-hour, 50 mph cruise followed by a 5-minute idle; and 5 successive EPA congested Freeway Driving Schedule Cycles, each followed by a 5-minute idle. Few test results meet all three regulated emissions standards, and the carbon monoxide standard is the one exceeded most often. The test results indicate a correspondence between high FTP carbon monoxide emissions and high idle carbon monoxide. The sulfate emissions are shown to be inversely related to the carbon monoxide emissions. The average sulfate emission value for the entire fleet was 2.7 mg/mi. Sulfate emissions increase to 5.8 mg/mi when HC, carbon monoxide, and nitrogen oxide regulations are met. Two types of sulfur dioxide emissions have been observed. In vehicles with low-idle carbon monoxide values, insignificant sulfur dioxide emissions occur during idle; in vehicles which have a high carbon monoxide value, a short burst of sulfur dioxide accompanied by a strong sulfur odor occurs upon deceleration.

Results of tests to determine the effect of mileage on emissions indicate that HC emissions increase from 1.1 gm/mile to 2.0 gm/mile after 20,000 miles and that carbon monoxide emissions increase with mileage. But sulfur dioxide purge behavior has not been found to be a function of mileage, and no overall correlation between mileage and sulfate emission is presently apparent.

The vehicle tests have also revealed that emissions patterns vary markedly according to vehicle manufacturer and that idle mixtures are frequently enriched, creating idle carbon monoxide levels higher than manufacturers' specifications.

III. CURRENT STATUS

A. Animal Studies

Since its inception in 1974, the Catalyst Research Program has sponsored work concerned with the effects of animal exposure to several pollutants. During the calendar year of 1976, the pollutants receiving major emphasis were sulfuric acid, manganese, and platinum. A summary of the major accomplishments in the studies of these pollutants follows:

1. Sulfuric Acid

The first set of experiments focused on the immune system, investigating the effects of sulfuric acid (H_2SO_4) mist on host defense mechanism. The animals were exposed to 1 mg/m^3 ($0.3 \text{ }\mu\text{m}$ – $0.5 \text{ }\mu\text{m}$) for various time periods.

The cell-mediated immune function of circulating lymphocytes was examined in male New Zealand white rabbits. The animals were assayed pre- and post-exposure so that each animal could serve as its own control. The animals were exposed for 2 hours per day to either clean filtered room air or to sulfuric acid. Using a modified microtechnique (1), the transformation of T cells was measured by culturing lymphocytes for 3 days in the presence or absence of $0.5 \text{ }\mu\text{g}$ purified phytohemagglutinin (PHA)/well, a lectin that specifically induces blastogenesis of T cells. During the final 24 hours, all cultures were pulsed with tritiated thymidine ($0.5 \text{ }\mu\text{Ci}$ /well). The extracellular label was removed and acid-precipitable protein collected on filters using a MASH III. With a scintillation counter, incorporation of tritiated thymidine was determined and data collected as counts/minutes.

For analysis, the data for each individual animal were converted to ratios. Table 1 gives the mean and standard error of these ratios. The analysis indicated that no significant alterations resulted from a single 2-hour exposure to air or sulfuric acid or from a 2-day exposure (4 hours/day) to air. However, lymphocytes of animals exposed to sulfuric acid for 4 hours/day for 2 days, showed a marginally significant ($p < 0.1$) increase in transformation, an increase that was similar in cells cultured both with and without PHA. This finding suggests the possibility that sulfuric acid enhanced the blastogenesis of T cells independent of PHA stimulation, or that sulfuric acid caused an alteration in the ratio of B:T cells.

To examine the humoral immune system, female Swiss white mice (strain CD-1) were exposed either to air or to sulfuric acid mist prior to an intraperitoneal immunization with sheep erythrocytes. Four days later, the spleens were removed for determination of the number of specific antibody (IgM) producing spleen cells using a modification of the Jerne hemolytic plaque technique (2). The data were analyzed as previously described. Acid mist caused no statistically significant effect (Table 2).

Because hematological changes were observed during the immunological investigation, experiments were conducted to quantitate these responses. One group of rabbits was exposed, for a single 2-hour period, to acid mist; a second group was exposed for the same length of time to air. Using analysis of variance, the decrease in hematocrit that occurred following exposure to sulfuric acid was found to be statistically significant ($p < 0.05$). Table 3 presents the data resulting from this experiment.

TABLE 1
Effect of H₂SO₄ on Lymphocyte Transformation

Exposure Regimen	Post-/Pre-Exposure			0.5/0.0 μ g	
	Number of Rabbits	0.0 PHA	0.5 μ g PHA	Pre-Exposure†	Post-Exposure† (Post - Pre)‡
Clean Air x 2 hrs	13	1.33±0.21	1.31±0.33	7.40±0.18	6.34±.97 -1.06±0.90
1 mg H ₂ SO ₄ /m x 2 hrs	8	0.95±0.18	0.86±0.18	5.75±1.30	4.70±1.30 -1.05±0.87
Clean Air x 4 hrs x 2 days	6	1.54±0.20	0.89±0.05	10.15±3.62	5.24±1.29 -4.92±2.36
1 mg H ₂ SO ₄ x 4 hrs x 2 days	9	2.19±0.67*	2.61±0.89*	9.58±2.19	13.68±5.40 4.10±4.88

*Reject H₀: $\bar{X} = 1$ at $p < .10$

†Reject H₀: $\bar{X} = 1$ at $p < .05$ for all means

‡Fail to reject H₀: $\bar{X} = 0$ for all means

TABLE 2

Effect of H₂SO₄ Mist on Number of Antibody-Producing Spleen Cells

Treatment (2 hr)	n	Log ₁₀ Plaques/10 ⁶ Cells
Air	24	2.80
1 mg/m ³ H ₂ SO ₄	25	2.74

TABLE 3

Effect of H₂SO₄ Mist on Hematocrit

Treatment (2 hr)	n	Hematocrit (pre- and post-exposure)
Air	8	0.75 ± 0.59*
1 mg/m ³ H ₂ SO ₄	16	2.19 ± 0.59

*Mean ± s.e.

Also, the number of leukocytes and their classification were determined, using a hemocytometer and differential counting of Wright's stained smears. Data were analyzed with analysis of variance. There was no statistically significant effect on the number of leucocytes per cubic centimeter. Figures 1 and 2 show the results obtained in a comparison of pre- and post-exposure response in animals exposed to air and those exposed to sulfuric acid, the number and percent of polymorphonuclear leucocytes (PMN) increased ($p < 0.05$), while the number and percent of lymphocytes decreased ($p < 0.05$). In the animals exposed to sulfuric acid, the decrease in percent lymphocytes and the increase in the total number of PMN's was greater ($p < 0.05$) than the changes found in the air-exposed control animals. These data indicate the possibility that there was some type of nonspecific stress (as evidenced by the air-exposed animals) which was enhanced by sulfuric acid.

Another subject of investigation was the extent to which the combined action of ozone and sulfuric acid aerosol affects host susceptibility to an aerosol of viable microorganisms (3). Observations of mortality in this streptococcal infectivity system are thought to represent the result of several subtle effects of pollutants on respiratory defense systems--namely, mucociliary clearance, the alveolar macrophage, and the immune system, suggesting the complexity of the model as observed by increased mortality rates, occurred following 2-hour inhalations of $> 2.0 \text{ mg Mn/m}^3$ for the insoluble manganous-manganic oxide atmospheres and $> 3.2 \text{ mg Mn/m}^3$ for soluble manganese chloride aerosols (Figure 3). These data were substantiated by the streptococcal clearance as shown in Figure 4. In animals exposed to manganese, the lungs were cleared of the streptococcal infection more slowly, and subsequently, the inhaled streptococci increased more in the manganese-exposed animals than in the infected control animals. For 15 days following infection, a significant reduction in the mean survival rate was observed in mice exposed to the particulate atmosphere, though not in mice exposed to the soluble aerosol ($> 5.25 \text{ mg Mn/m}^3$). The decrease in percent survival from the control response at these concentrations varied from a 12.5 percent decrease for those exposed to the soluble aerosol to 21.7 percent for those exposed to the particulate atmosphere. Exposure to ozone (0.196 mg/m^3) was for 3 hours, while exposure to sulfuric acid lasted for 2 hours. Neither pollutant alone caused a significant increase in mortality compared to controls exposed only to clean air. Figure 5 shows the increase in mortality for each treatment group. In those studies involving the sequential action of the two pollutants, the treated group experienced a statistically significant increase ($p < 0.05$) in respiratory infections over controls (indicated by percent mortality) only when the exposure to ozone immediately preceded exposure to sulfuric acid. When this order of exposure was followed, the observed mortality was equal to the additive effect of the individual pollutants. The two combined exposure groups were not significantly different.

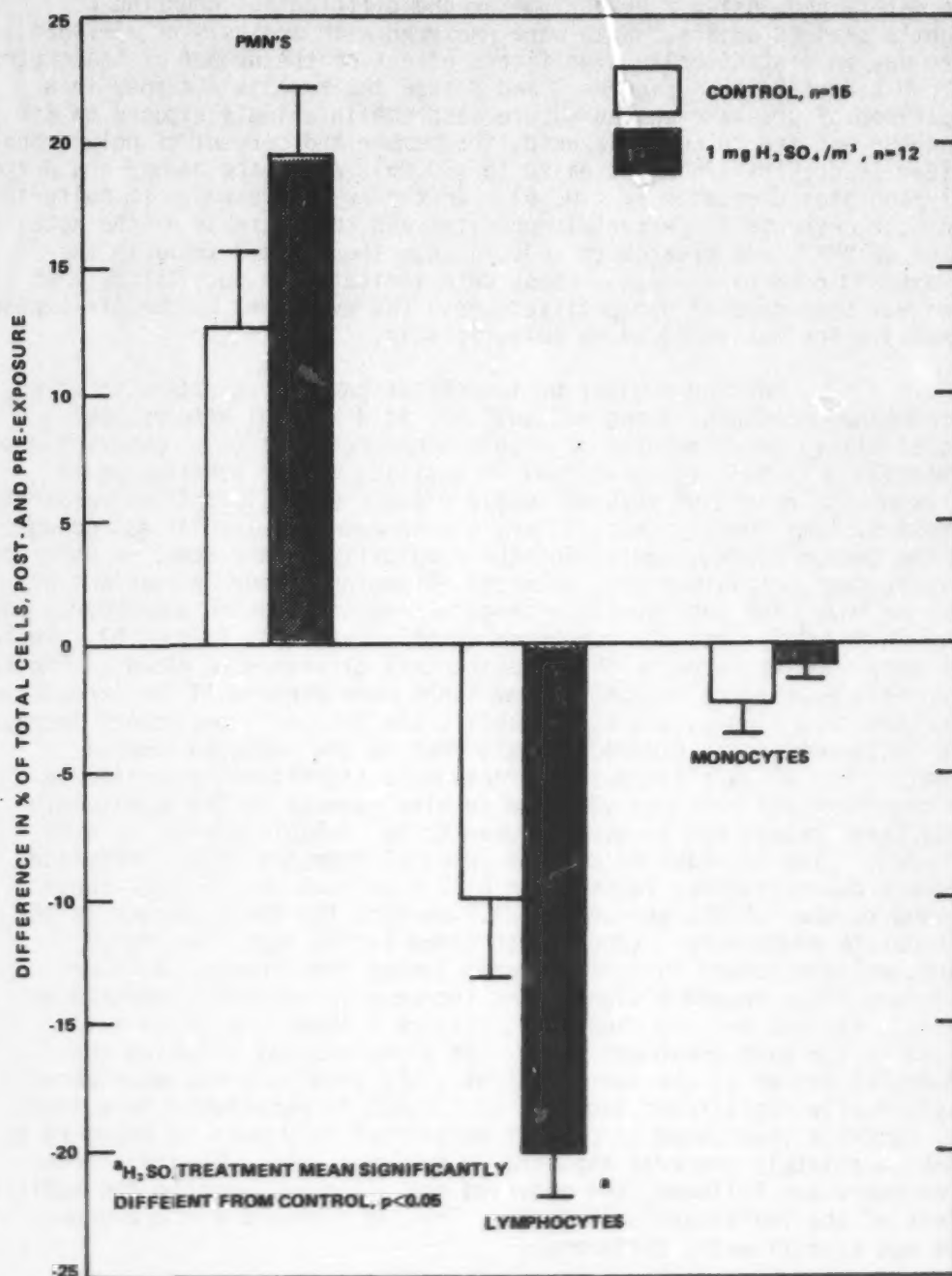


Figure 1. Effect of a 2-hour exposure to sulfuric acid mist on percentage of circulating polymorphonuclear leucocytes (PMI's), lymphocytes, and monocytes.

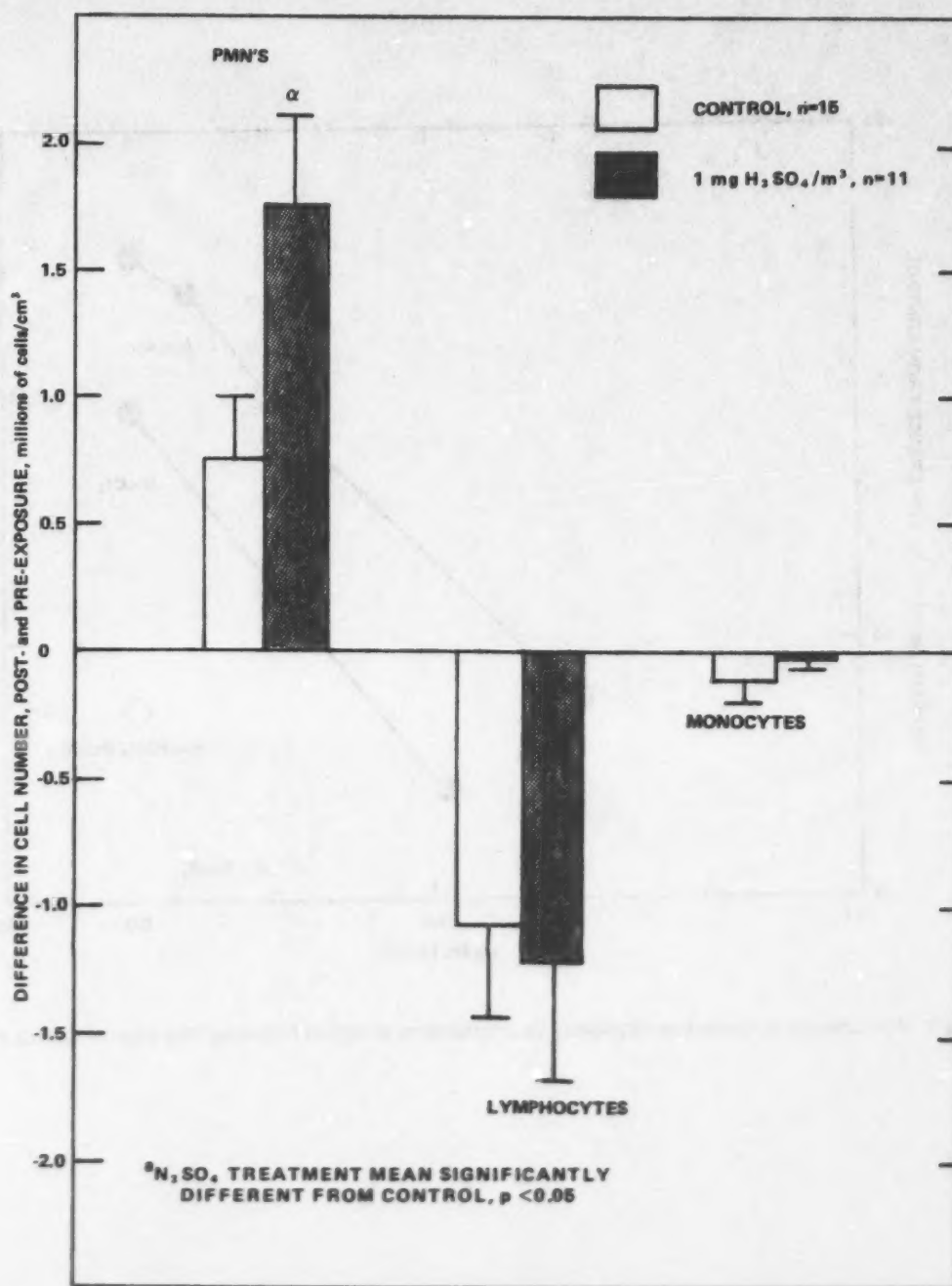


Figure 2. Effect of a 2-hour exposure to sulfuric acid mist on numbers of circulating polymorphonuclear leucocytes, (PMN's), lymphocytes, and monocytes.

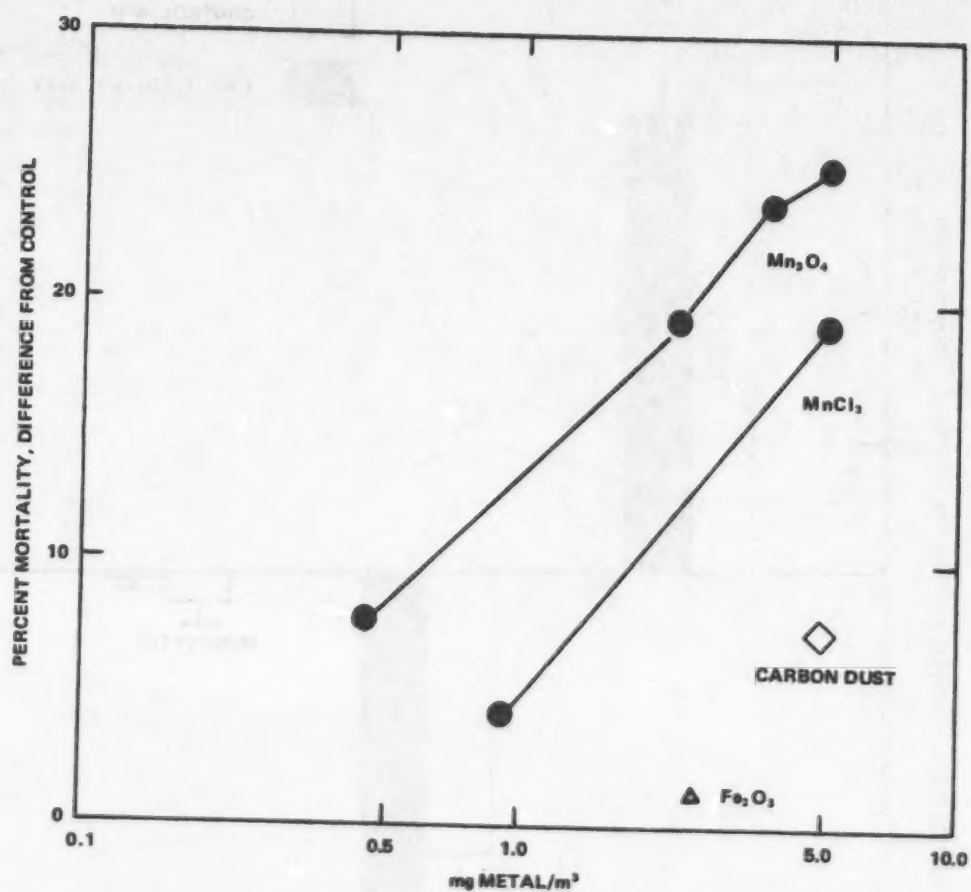


Figure 3. Alteration in pulmonary susceptibility to streptococcal infection following inhalation of various metals.

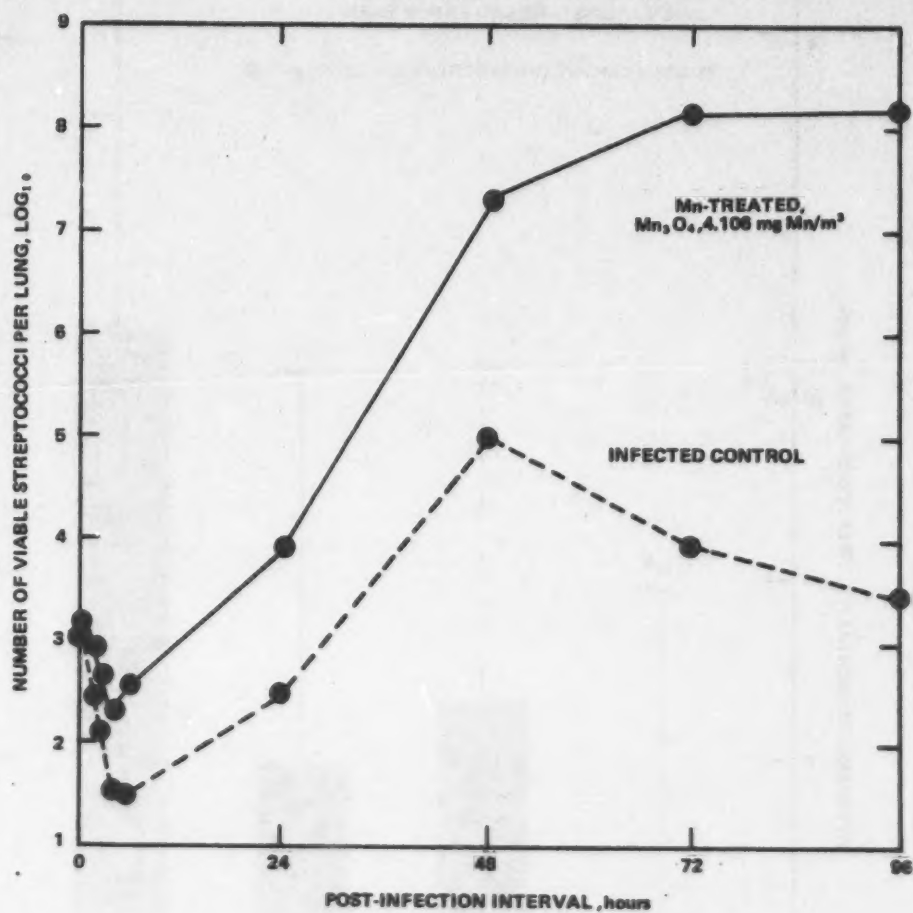


Figure 4. Effect of manganese inhalation on the growth and clearance of streptococci in mouse lungs following infection.

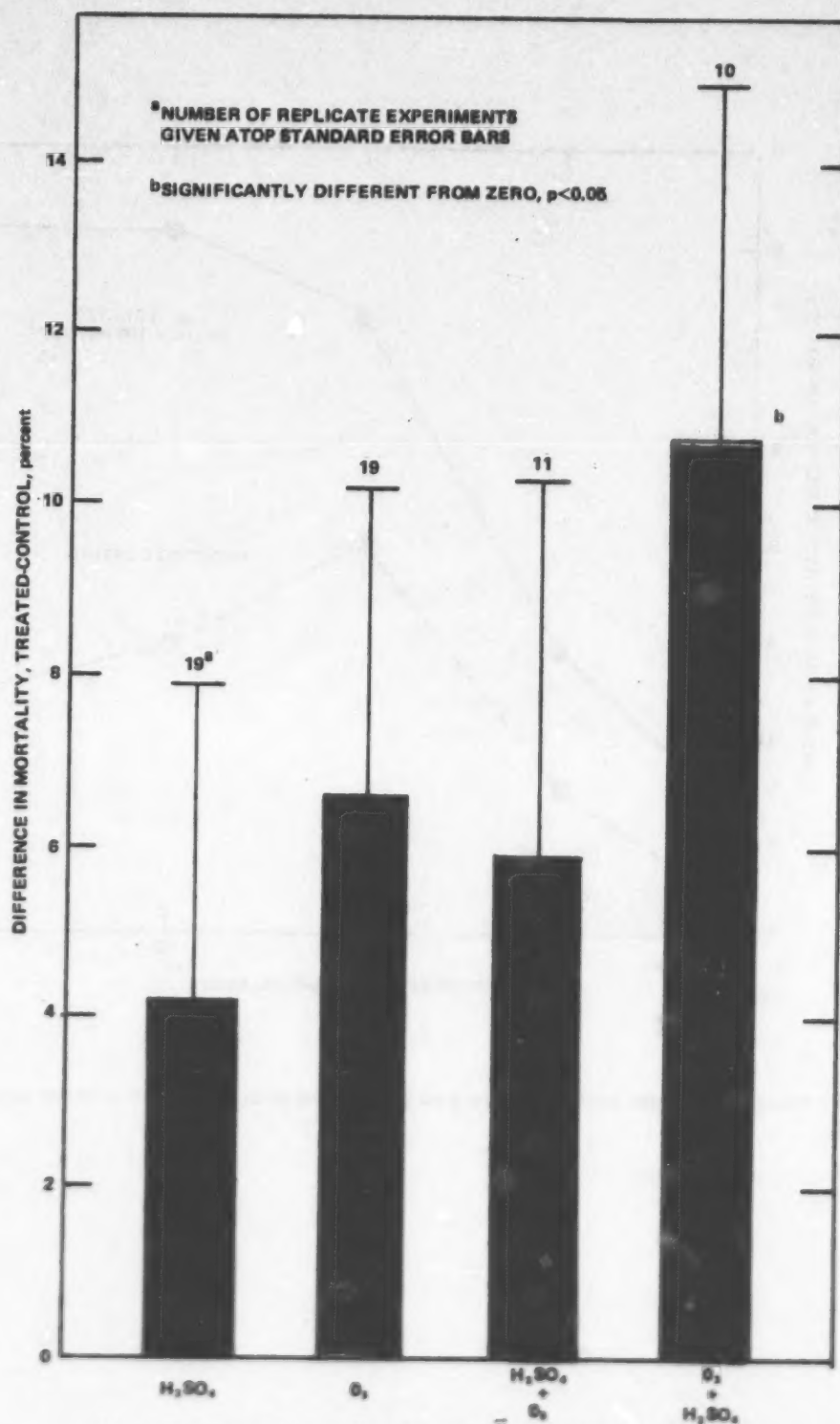


Figure 5. Increase in mortality after exposure to sulfuric acid and to ozone.

It is particularly interesting that the sequence of exposure to these two chemicals is a factor in determining the toxicity. It is unlikely that the difference is a spurious result, since the number of experimental replications and animals tested were adequate, based on the results of previous studies using this model system. From these data, one can postulate that the effect on the host's pulmonary defense system or on pulmonary function parameters is of greater magnitude when ozone is administered prior to sulfuric acid. A possible explanation of the differences between the sequential exposure regimens may be related to altered frequency and depth of respiration of the test animals. It is more likely, though, the exposure to ozone initiates biochemical and physiological changes in the tissue which result in increased sensitivity to sulfuric acid. This may lead either to larger deposits of sulfuric acid, causing a greater acid dose to sensitive target tissue, or to deeper penetration into the respiratory tract. To determine whether sulfuric acid and ozone could also influence the mucociliary escalator, which is responsible for clearing and conducting airways of any materials that impact upon the mucous layer, additional studies were performed. Hamsters were exposed to 1 mg/m³ sulfuric acid for 2 hours. Immediately, and at 24 and 48 hours post-exposure, ciliary beating was significantly depressed ($p < 0.05$). After 72 hours of recovery in clean air, beating frequency has approached control values. Lower concentrations (0.5 mg/m³) of sulfuric acid had no statistically significant effects. Hamsters exposed to 0.196 mg/m³ ozone for three hours exhibited no alterations of ciliary beating. When the animals were exposed for three hours to .196 mg/m³ ozone, immediately prior to a two-hour aerosol of sulfuric acid (1 mg/m³), the observed depression in ciliary beating was that which would be expected from acid alone.

More research involving sulfuric acid has recently been initiated. The objective of a study begun in the fall of 1976 is to provide information about the way metallic sulfates, sulfur dioxide (SO₂), and sulfuric acid can alter respiratory defense mechanisms, particularly the alveolar macrophage. The work is being conducted under an EPA grant to the School of Public Health, Harvard University. The principal investigator is Dr. Joe Brain. Only preliminary experiments have been conducted thus far.

2. Metals

a. Manganese

The next area of emphasis in EPA's animal exposure experiments in the CRP involved inhalation studies of acute exposures to respirable manganese (Mn) aerosols. These were performed in conjunction with a laboratory-induced streptococcal infection. Utilizing this infectivity system (4) in mice, studies were conducted to elucidate the relation-

ship between manganese inhalation and chronic respiratory disease. Two manganese sources were selected for this study: soluble manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) and insoluble manganous-manganic oxide (Mn_3O_4).

Manganese aerosols ($< 2 \mu\text{m}$) were generated within an aerosol exposure apparatus. The fluid atomization generating system was used with the manganese chloride. The particulate aerosol generating system was utilized with manganous-manganic oxide.

Mouse exposures were performed as single acute exposures of two hours duration. Specific exposure parameters, such as total particle counts and temperature/relative humidity measurements, were continuously monitored throughout the exposure period. Manganese quantitation, both during the exposure and during tissue deposition, was performed using atomic absorption spectrophotometry (A.A.).

Differences were noted in pulmonary deposition and subsequent clearance between the soluble manganese chloride aerosols and the insoluble, particulate manganous-manganic atmospheres (Figure 6 and Table 4). These differences are apparently due to variations in aerosol particle size and perhaps to the solubility of the particles. The mass median diameter (MMD) of manganese chloride aerosols was routinely $< 2 \mu\text{m}$, whereas for manganous-manganic oxide the MMD was $< 1.2 \mu\text{m}$. These data suggest enhanced deposition by the manganous-manganic oxide atmospheres as was observed.

Carbon black and iron oxide particles did not exhibit toxic effects in the infectivity system. These data seem to substantiate the occurrence of true metal toxicity rather than physical irritation by the particulate nature of test atmospheres.

b. Platinum

As reported in the Second Annual Catalyst Research Program Report, and in the 1975 Platinum Research Review Conference proceedings, that portion of the Catalyst Research Program which relates to platinum, palladium, and other noble metals is declining in emphasis with relation to the total program effort. Most extramural projects have been completed or are nearing completion. There are a few studies, however, which are still active at this writing; a brief summary of the status of the projects follows.

One study now nearing completion is an investigation of whether a hypersensitive state (immediate and/or delayed) can be induced in experimental animals exposed to platinum or palladium metals under various conditions. This work, carried out at St. Vincent College, Latrobe, Pennsylvania, has shown that platinum alone or in the complexed

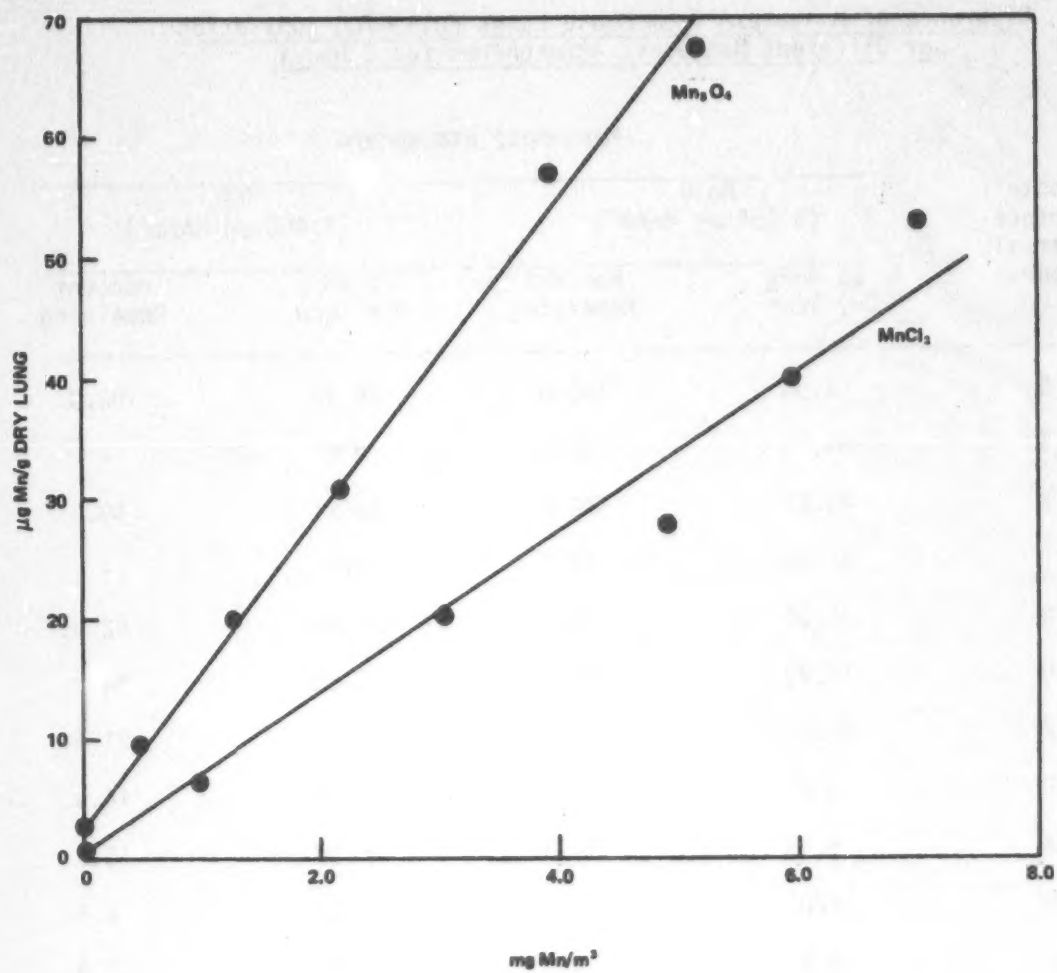


Figure 6. Manganese deposition immediately after inhalation of various aerosol concentrations in mice.

TABLE 4

Clearance of Manganese from Mouse Lungs Following Inhalation
of Different Manganese Atmospheres for 2 Hours

Post- exposure Interval, Hours	Manganese Atmosphere			
	Mn_3O_4 (3.654 mg Mn/m ³)		$MnCl_2$ (7.468 mg Mn/m ³)	
	$\mu\text{g Mn/g}$ Dry lung	Percent Remaining	$\mu\text{g Mn/g}$ Dry lung	Percent Remaining
0	54.94	100.0	48.90	100.0
1	51.15	93.1	N/D	-
2	42.02	76.5	29.21	59.7
3	31.70	57.7	N/D	-
4	26.91	49.0	20.83	42.6
6	15.99	29.1	16.95	34.7
12	10.27	18.7	10.53	21.5
18	N/D*	-	7.30	14.9
24	6.78	12.3	6.39	13.1
30	N/D	-	4.28	8.8
36	N/D	-	3.86	7.9
48	4.32	7.9	2.71	5.5
Control	2.15	-	2.53	-

*N/D, not determined.

state (i.e., with egg or guinea pig albumin) will not induce any type of allergy. Palladium alone is also without effect; however, palladium, when complexed with albumin, will induce a delayed allergy which can be transferred to normal recipients via spleen cells from sensitive donors. A final report on this project is scheduled for Spring of 1977.

Platinum or platinum sulfate [$\text{Pt}(\text{SO}_4)_2$] was the compound selected for study in a series of experiments assessing the use of leucocyte metabolism as an indicator of health effects as expressed in a number of subtle biochemical and physiological changes. Three separate studies are being undertaken: alteration of leucocyte metabolism and chromosomal aberrations; alteration of platelet metabolism, immunological response, and PMN neutrophil phagocytosis; and enzyme changes in the liver, kidney, and heart. In addition, histamine and serotonin levels are monitored in blood and urine. All three studies use rabbits exposed to a high and low dose of platinum sulfate except in a limited portion of the *in vitro* chromosome work, where a limited study of human blood cells of nonexposed individuals is included for comparative purposes. This effort is still underway at Stanford Research Institute, but preliminary results indicate that platinum sulfate appears to have little or no effect on the parameters measured, with the exception of its activity as a severe eye irritant. Also, recent preliminary work suggests that the sulfate may also have some cytogenetic activity. A final report is expected in late 1977.

The biological activity of platinum, specifically the metallic oxide (PtO_2) in the induction of pulmonary neoplasia by benzo(a)pyrene is the subject of a 3-year study nearing completion at the State University of New York at Stony Brook. The actions of lead oxide (PbO) and iron oxide (Fe_2O_3) in the same system are being examined for comparison. In addition, the role of platinum or lead in changes of transpulmonary absorption, pulmonary clearance, and pulmonary response to intrapulmonary particulates, is being examined. The study utilized both intratracheal instillation and cutaneous application. Necropsy of animals from early exposure groups is now being performed. No results are yet available in early 1978.

Platinum sulfate is one of several trace substances being evaluated at the State University of New York at Buffalo for effects in major metabolic pathways in the central nervous system. Biotransformation of trace substances in a developing embryo-fetus animal model and in an adult model is being determined as well. The study will also examine the correlation of these two efforts with those of selected behavior in the adult and during postnatal development of offspring of treated mothers in appropriate models. The purpose of these studies is to identify biochemical indicators of exposure to trace substances such as platinum. The

resulting biochemical changes will be correlated with changes in behavior to increase understanding of the ways in which these substances interact with mammalian systems. Preliminary results to date indicate that platinum (as the sulfate) has an effect on behavior which may be characterized as moderately depressive. Final results on the portion of the grant dealing with effects of platinum should be available in late 1977.

Work at Lawrence Livermore Laboratory has established that platinum in the form of either platinum sulfate or potassium hexachloroplatinate (K_2PtCl_6) can, under laboratory conditions, be methylated by reaction with methyl B_{12} (methylcobalamin) in the same way in which mercury is methylated. Ability of other metals to be methylated by this means has also been studied and was reported in the first and second Annual Catalyst Research Program Reports. The emphasis of current research is on two areas: (1) further chemical characterization of one MePt compound prepared from K_2PtCl_6 and MeB_{12} and isolation and characterization of MePt products from the reaction of $Pt(SO_4)_2$ with MeB_{12} , and (2) studies of the cellular toxicity and mutagenicity of at least one MePt compound as well as several related Pt-salt complexes. In vitro biological experiments will employ Chinese hamster ovary cells as a mammalian test system. It is anticipated that final results of this research will be reported in late 1977 or early 1978.

Evaluation of analytical methods for measuring trace elements in biological matrices (especially mammalian tissue) is the subject of a project in progress at Stewart Research Laboratories. Existing analytical methodology for platinum, as well as for palladium, nickel, manganese, chromium, cerium, and vanadium, is being reviewed through a thorough literature survey. A series of reports will document (1) the various limits of detection achieved; (2) preconcentration, separation, and extraction techniques; (3) sources of contamination; and (4) other considerations necessary in order to recommend the most promising of those methods developed, applied, and reported to date. A limited laboratory evaluation of one or more of the methods recommended on the basis of the literature is planned for late 1977 and will be reported in early 1978. The reports on methods for individual metals should be available late in 1977. It is anticipated that this series of reports will be valuable to researchers in the area of trace metals, especially where measurements of extremely small amounts of metal in tissue samples are necessary for interpretation of experimental results.

In 1975, the Catalyst Research Program held a review conference on the platinum research sponsored by the program. A report of the conference was published in early 1976 as "Proceedings - Catalyst Research Program Platinum Research Review Conference." Since all research

under the CRP which is related to platinum and noble metals is scheduled for completion within the next eighteen months, a followup report is planned to summarize final results of all aspects of the program. Since platinum is an element which had received little attention either in analytical or toxicological research prior to the establishment of the CRP, it is expected that this summary report will become an extremely useful reference for future researchers in this field. The report is scheduled for publication in late 1978.

B. Human Studies

1. Objectives

The CRP, as part of its intensive research on health effects of sulfuric acid, is planning to initiate early in 1977 at its Chapel Hill, N.C., facility, a study of human exposure to sulfuric acid. A summary of the project and a detailed description of facilities and procedures follow.

This proposed research seeks to investigate in young healthy male volunteers the potential health effects of low-level sulfuric acid aerosols in a concentration range of 50 to 200 $\mu\text{g}/\text{m}^3$ with a mass median diameter (MMD) particle size in the range of 0.05 to 0.5 micrometers.

It is estimated by EPA that the peak urban atmospheric burden of sulfuric acid aerosol is at present in the range of 20 $\mu\text{g}/\text{m}^3$ and that the widespread use of automobile catalytic converters might increase this level. The catalytic converter produces a sulfuric acid aerosol via the generation of sulfuric acid within the converter. There is little definitive information presently available as to the health effects dose response curve for sulfuric acid aerosol concentrations in this range and size.

Sulfuric acid aerosol refers to a suspension of sulfuric acid droplets in air. Under some conditions in the ambient atmosphere, sulfuric acid aerosol has limited stability and may exist only briefly in its original chemical and physical form. For example, the aerosol can be neutralized by interaction with ambient atmospheric ammonia. Sulfuric acid particles are hygroscopic and increase in size when the humidity is high. Sulfuric acid aerosol is one of several airborne particulate sulfates which may be found in ambient air.

Particle size is a crucial factor in sulfuric acid aerosol toxicity because it is a major determinant of the deposition site within the respiratory system (5). The hygroscopic and irritant potential of sulfuric acid aerosol may alter the normal rate of regional particle deposition under certain circumstances. Since particle size influences deposition and since deposition is important to the relative toxicity, size characterization is essential in the assessment of the health impact of

of sulfuric acid aerosol exposure. Mass median aerodynamic diameter (MMAD) is a necessary but not a fully sufficient measure of aerosol particle size. In addition to MMAD, a measure of the variability of the particles or frequency distribution, such as range or standard arithmetic or geometric deviation, is also desirable. Aerosol characterization has been deficient in some studies described in the literature.

2. Previous Studies

Animal toxicology, clinical studies, and epidemiologic studies were reviewed extensively by Battigelli and Gamble (6), Lewis, et al. (7), and by Ariey, et al. (8). Data on sulfuric acid toxicity in humans are more limited than animal data, but there is some information on short-term exposures. Sulfuric acid is detected by human subjects at about 500 $\mu\text{g}/\text{m}^3$ (9). At higher concentrations, there is a spectrum of responses ranging from increased air flow resistance to acute irritation of mucous membranes, lacrimation, and coughing (7).

Toyama, et al. (10) have reported an increase of 18 percent in pulmonary flow resistance in humans with H_2SO_4 exposure as low as 10-100 $\mu\text{g}/\text{m}^3$ with a particle size 1.8 μm count median diameter (CMD). At 800-1400 $\mu\text{g}/\text{m}^3$, with 4.6 μm (CMD) particles, airway resistance was increased by 36.5 percent. In these experiments: (1) sulfuric acid aerosol was produced by combining hydrogen peroxide and sulfur dioxide in a mixing chamber; (2) particle size was determined by impacting the acid aerosol on a thymol-blue impregnated strip and microscopically measuring the size of the resulting circular red spots; and (3) flow resistance was measured by use of the interrupter technique. The use of these techniques has been criticized by independent reviewers who have stated that, as a result of the methods used, Toyama's conclusions are of questionable value (7).

Amdur, et al. (11) have reported that respiratory rates have increased by about 30 percent, depth of breathing decreased by about 28 percent, and maximum inspiratory-expiratory flow rates decreased by about 20 percent at a concentration of 350-500 $\mu\text{g}/\text{m}^3$. These concentrations are below subjectively detectable levels. The ventilatory parameters changed in a nonlinear fashion with 80 percent of the changes occurring during the first 3 minutes of exposure. The initial phase of the recovery period was almost a mirror image of the exposure period, i.e., nonlinear rapid return to normal values, with the fastest return in the first 3 minutes. As demonstrated in animal studies, such rapid and marked changes are reflex in nature. Although the airway resistance was not measured, its characteristic increase can be easily observed on a number of air flow tracings shown in Amdur's publications. It also appears that as the H_2SO_4 concentration increases, so do respiratory rate and air flow resistance.

Amdur has shown that in humans the average retention of inhaled sulfuric acid varies from 50 percent to 87 percent with exposure to 400 to 1000 $\mu\text{g}/\text{m}^3$ of sulfuric acid aerosol. As the respiratory rate increases, which occurs at somewhat higher levels of sulfuric acid aerosol, the percent retention is reduced, possibly indicating a protective response at these levels (11). All of the subjects involved in the clinical studies reported above were healthy young adults who could easily compensate for the increased resistance imposed upon their breathing.

Recently, Hazucha and Bates (12) have shown synergism between ozone and sulfur dioxide, as measured by dynamic lung function tests in man. They postulated that the two gases interact rapidly on the large, wet, air-tissue interface of the lung, covering the inner surface with sulfuric acid. These results suggest that both peripheral and central airways are affected, but more detailed studies are needed to determine the mechanism responsible for these changes.

All the above studies were performed using healthy human subjects. No studies on subjects with pre-existing disease have been attempted to date.

3. Methodology

The generation and monitoring of these concentrations and size of sulfuric acid aerosol are technically difficult and are therefore covered in an attachment which describes the design plan and operating protocol of the facilities for the controlled exposure of humans to sulfuric acid aerosol.

A single blind protocol will be employed, using young healthy male volunteers between the ages of 19 and 30. Judging from the past literature, it would seem possible to use a double blind protocol in that the subjects should not sense acid aerosols at these concentrations. This permits study observation without the subject's awareness of the exposure conditions and without investigator's prejudice. The exposures are to take place in the CSD Lexan Chamber, which has been used for the ozone exposures. The levels to be studied initially would be 50 and 200 $\mu\text{g}/\text{m}^3$ with a MMD particle size controlled in the range of 0.05 to 0.5 μm .

For this study, the subjects will be exposed to acid aerosol for 2 hours. There is some concern that adaptation may occur quickly and that longer exposures are unnecessary. It is expected that such a 2-hour protocol could be accomplished in a double-blind, randomized fashion such that the subjects could be studied over several days with the control days randomized with the exposure day. In this manner, as many as two to three subjects could be studied per week, with one subject following the other in succession. The exact design of this random protocol will depend on subject availability.

It will also be important to determine whether there are any lasting effects which would carry over from one day to the next, but the literature does not suggest this. The protocol is outlined in Tables 5 and 6.

When the subject enters the chamber, baseline determination of all parameters will be made. He will be exposed 45-60 minutes later. At the end of 5, 10, and 15 minutes of exposure, resting tidal volume will be recorded. After an additional 15 minutes of exposure, all of the appropriate parameters will be remeasured. A comparison of the readings at 15 minutes and 30 minutes of exposure will allow us to observe whether adaptation or further effects of the exposure has occurred. After 5 minutes of rest, the subject will begin an exercise program of approximately 15 minutes, taking him up to 50 minutes. The exercise will be performed on a bicycle ergometer at a workload of 700 kg/min, an exercise level that produces approximately a doubling of heart rate, to evaluate the effect of stress in combination with acid aerosol exposure. A similar 15 minutes of exercise will be performed prior to completion of 2-hour exposure. Immediately following the 2-hour exposure, the whole battery of tests used during baseline measurements will be determined.

The test parameters will primarily be measurements of pulmonary function since the limited literature suggests this as the most important area of change. The following measurements will be taken.

- a. FVC - forced vital capacity
- b. FEV₁ - forced expiratory volume in one second
- c. MMFR - mid-maximal expiratory flow rate
- d. FERV - forced expiratory reserve volume
- e. V₅₀ - peak flow at 50 percent of forced vital capacity
- f. V₂₅ - peak flow at 25 percent of forced vital capacity
- g. R_{aw} - airway resistance
- h. FRC - functional residual capacity
- i. TLC - total lung capacity computed from adding FVC to RV

In addition to the studies of pulmonary function, a single lead precordial ECG will be continuously recorded while the subject is in the exposure chamber, either on controlled days or on exposure days. This is part of the subject safety, but, in addition, the ECT signal provides an indication of change in heart rate with exercise or as a result of exposure under resting conditions. It also provides an opportunity to observe any arrhythmogenic potential of the exposure. The ECG is not seen as a primary investigative tool but as one which insures monitoring for subject safety reasons.

TABLE 5

Blind Exposure Protocol for H₂SO₄ AerosolExperimental SessionsIntervention Sequence I: Control, Control, Exposure (CCE)

Time	Session 1	Session 2	Session 3
	Control (C)	Control (C)	Exposure (E)
8:30 a.m.	Pre-exposure Evaluation and Sampling	Same	Same
9:30 a.m. to 11:00 a.m.	Lexan Chamber Clean Air	Lexan Chamber Clean Air	Lexan Chamber H ₂ SO ₄ Aerosol 100 µg/m ³ , 0.05-0.5 µg particle size
11:30 a.m.	Post-exposure Evaluation and Sampling	Same	Same

Intervention Sequence II: Control, Exposure, Control (CEC)

Control (C)	Exposure (E)	Control (C)
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Same daily procedure as for CCE.

TABLE 6

Time Course for Each of the Three Experimental Sessions

Baseline Evaluation	8:30 a.m.	Baseline Pulmonary Function Studies (PFS)
Enter Lexan Chamber	9:30 a.m.	
Sitting Quietly	9:35 a.m. 9:40 a.m. 9:45 a.m.	Resting V_T After 5-, 10-, 15-Minute Exposure
Exercise Bicycle Ergometer for 15 Minutes	10:05 a.m.	
Sitting	10:30 a.m.	Resting PFS After 1 Hour of Exposure
Exercise Bicycle Ergometer	11:05 a.m.	
Leave Lexan Chamber	11:45 a.m.	2nd Post-exercise PFS After 2 Hours of Exposure
Post-exposure Evaluation	Subject will complete a short symptom questionnaire before and on leaving the chamber during each experimental session.	

After each experimental session, the subjects will complete a subject symptom inventory questionnaire to determine what specific symptoms, if any, they experienced in conjunction with the experimental session.

Approximately 12 adult healthy young non-smoking male volunteers are to be studied. It is anticipated that most will be student volunteers and other young men from the Chapel Hill community. Each potential subject will be given a history and physical examination before being selected as a normal healthy volunteer. In addition, a hematocrit, white blood cell count, and differential will be obtained. Subjects are to be carefully questioned to exclude those taking any medications, those with any recent pulmonary infections, etc. Temperature, blood pressure, pulse, and respiration are to be recorded just prior to starting the experiment. An informed consent form describing the study will be signed by each subject prior to his participation.

It is anticipated that there will be very little risk to the healthy male subjects with a 2-hour exposure to these low levels of sulfuric acid aerosol. It is also anticipated that it will be difficult to measure any detrimental health effects in any of these parameters at this low level; the industrial human exposure level or standard is set tenfold higher at 1 mg/m³. The only benefit to the subjects is a medical examination and routine pulmonary function testing.

The LEXAN Chamber facility at present will permit the evaluation of 2 subjects per week. The evaluation of at least 12 subjects is anticipated. Although a double-blind protocol is considered to be highly desirable in terms of the statistical analysis, a single-blind protocol control-exposure-control (CEC) was selected. Since the two groups of investigators (monitoring group and physical testing group) work rather independently, the double-blind design is considered unnecessary for this pilot study. From a statistical point of view, a CEC protocol will permit the population sample for this pilot study to be kept at a minimum. A three-way analysis of variance was considered the most suitable test for a comprehensive analysis of the data. In this way, variance between individual days and/or hours as well as subjects can be tested more effectively. Other statistical tests may be employed in analyzing the data to test alternate hypotheses. In addition to on-line computer analysis, all records will be analyzed manually by one of the investigators to assure quality of the data. All data will be reduced and statistically analyzed by computer using standard statistical packages, e.g., SSPS.

C. Mobile Source Emissions

In cooperation with the New York State Department of Environmental Conservation at the Automotive Emissions Laboratory (AEL) in Albany, New York, the EPA is conducting a research project to measure the sulfate, particulate, and regulated emissions for a group of 49 in-use catalyst vehicles obtained from the fleets of several cooperating organizations and from private vehicle owners in the Albany area. The collection of data began in December 1975, and is projected to continue throughout 1977. This report is a summary document. More detailed results are available in monthly reports to the Project Officer, including the metals emissions indicated in Table 7.

1. Test Procedures

Each vehicle is tested periodically at intervals of approximately 5,000 miles to observe the effects of aging on emissions and on fuel economy. A particular sequence of test driving modes is followed:

- a 1975 Federal Test Procedure (FTP);
- a 1-hour, 50 mph steady cruise;
- five successive EPA Congested Freeway Driving Schedule cycles

The 1-hour, 50 mph cruise and the five CFS driving cycles are each followed by 5-minute idle periods with the vehicle transmission in neutral. This combination of test-driving modes results in an experimental sequence of approximately 125 miles which lasts over 4 hours per vehicle test. Table 7 shows the measurements that are made during each test segment. The AEL test bay is equipped with 30 tons of air conditioning (cooling, heating, dehumidification, humidification) providing 15,000 cfm of conditioned air through two parallel sets of multiple overhead registers directed down along both sides of the vehicle positioned on the dynamometer. With this system, room temperatures are typically held between 19°C and 24°C for all testing modes. A large fan is directed at the front of the vehicle and a squirrel cage blower is directed diagonally from the side of the vehicle ahead of the rear tires. This blower is located behind the converter to provide rear tire cooling in order to prevent tire failure.

Flow through the constant volume sampler (CVS) is approximately 400 cfm, and the in-line dilution tunnel closely follows the design of several similar tunnels in use by EPA laboratories. A clayton CTE-50 direct drive variable-inertia, automatic road-load missions dynamometer is used in all tests. Laboratory standard gases are cross-calibrated by EPA Ann Arbor. Sulfur dioxide is measured in dilute-filtered exhaust by a Lear-Siegler SM-100-second-derivative UV spectrometer. Sulfur dioxide mass emissions are

TABLE 7

Data List for Each Emissions Test

Test Segment	Measurements
Vehicle Check-In before 12-20 hour soak	Idle HC, CO; Engine Analyzer Check-in (ignition, timing, power, balance, EGR, etc.) Visual emission system integrity. Tank fuel sample: Sulfur, Lead, Phosphorous, Reid Vapor Pressure, API Gravity, Density, Distillation. Odometer, Engine hour meter, Totalizing fuel meter.
1975 FTP	Gaseous emissions: HC, CO, NO _x , CO ₂ , SO ₂ one 47 mm fluoropore filter for entire FTP: total particulate mass, soluble sulfate by Barium Chloranilate (BCA) SO ₂ trace in dilute exhaust and mass by continuous integration. O ₂ continous trace in raw exhaust.
1-Hour, 50 mph Cruise	Same as for FTP with 1 additional 47 mm fluoropore filter for Particulate Elemental Analysis by X-ray Fluorescence: Aiuminum, Phosphorous, Sulfur, Calcium, Iron, Copper, Bromine, Zinc, Platinum and Lead.
5-minute Idle Periods	SO ₂ trace, mass by continuous integration. Soluble sulfate mass by BCA from 47 mm filters collected: A) one filter for first idle after 50 mph cruise and B) last 3 idle periods averaged on single filter.
Five CFS Cycles Followed by 5-minute Idle Periods	Same as for FTP.

determined by continuous electronic integration of the output signal of the spectrometer. The optical chamber is thermostatically controlled at 50°C to prevent condensation. Dilute exhaust sulfur dioxide concentration is also recorded continuously on a strip chart recorder/disc integrator in order to observe the relationship of sulfur dioxide emissions to driving mode. Mass balance sulfur dioxide injection tests similar to propane tests for HC have verified the ability of this system to quantitatively detect sulfur dioxide, even in the presence of an auto exhaust background.

The collected particulate is analyzed for soluble sulfate by the semi-automated barium-chloranilate (BCA) technique. The apparatus is calibrated with prepared standards on a daily basis using a quadratic fit to low-range calibration points. Peak areas are integrated using a Columbia Scientific Supergrater II.

2. Characteristics of Vehicles Tested

Four cooperating institutional fleet operators provide vehicles. Privately owned vehicles are solicited by mailings to registered owners of 1975 and 1976 model vehicles in the Department parking lot. One vehicle (1975 Chevrolet Wagon, 454 V-8), is fueled and maintained by AEL staff to serve both as a control vehicle for testing and as an overnight loan car when privately owned vehicles are tested.

Vehicles are not screened before entry to the test group. Low-mileage vehicles are recruited when available, but no criteria of age or tune-up condition (idle carbon monoxide, etc.) are used to select or reject any vehicle. Vehicles are tested in "as received" condition after a thorough analysis of vehicle operating parameters. Tank fuel is used for testing whenever possible; commercial lead-free fuel is added at AEL prior to the test if the vehicle as delivered has insufficient fuel for the entire tests.

Tests are scheduled at 5,000-mile intervals when possible; however, scheduling constraints frequently dictate longer intervals, especially for high-mileage fleet vehicles. To date, 127 tests span approximately one million total miles for the 49 test vehicles. Over 90 percent of the tests are on cars with less than 28,000 miles. Six of these vehicles have had five or more tests, and five have had only one test. The remaining 38 vehicles have completed two to four tests at this time. The greater availability of larger vehicles for the project is reflected by the fact that only six vehicles in the test group have inertia weights less than 3,000 pounds. Table 8 gives a breakdown of the 49-car group and of the 127 FTP test data by manufacturer and by fleet vs. private owner.

TABLE 8
Classification of Cars and Tests

	General Motors	Ford	Chrysler
<u>49 Cars:</u>	18	9	22
24 Fleet Cars	(4)	(2)	(18)
24 Personal Cars	(13)	(7)	(4)
1 Control Car	(1)	(0)	(0)
1975 Model Cars	8	4	17
1976 Model Cars	10	5	5
<u>127 Emission Tests:</u>	50	18	59
76 Fleet Tests	(19)	(5)	(52)
46 Private Tests	(26)	(13)	(7)
5 Control Tests	(5)	(0)	(0)

3. Average Emission Results

Table 9 shows average emission results for all tests for various subclassifications, using the same subclassifications. Tables 10-12 show emission results for each manufacturer. CFS emissions values for individual tests are the average of the last three CFS cycles of each test. Test-by-test review of the sulfate emissions for the five CFS cycles in each test has shown that stabilized emissions values are achieved in most cases by the second CFS cycles and that the average of the last three cycles is an accurate measure of stabilized emissions.

In general, these results show low sulfate emissions and high carbon monoxide emissions. Idle carbon monoxide concentration and carbon monoxide mass emission data exhibit a direct correspondence. Few test results meet all three regulated emission standards, with the carbon monoxide standard being exceeded most often.

Emissions certification standards for 49 states for both 1975 and 1976 vehicles are as follows: 1.5 gm/mi HC, 15.00 gm/mi CO, and 3.1 gm/mi NO. Of the total 127 tests using 49 vehicles, 30 tests performed on 15 vehicles are at or below the standards for all 3 regulated pollutants.

a. Carbon Monoxide

Average carbon monoxide (CO) emissions for the 127 tests were 25.1 gm/mi, significantly above the 15 gm/mi standard (see Table 9). The average idle carbon monoxide concentration for the tests is 2.4 percent, compared to 0.4 percent for the 53 tests in which FTP carbon monoxide emissions are less than the 15 gm/mi standard. This correspondence of high FTP carbon monoxide emissions and high idle carbon monoxide is further indicated by grouping FTP carbon monoxide data according to a dividing point of 1 percent idle carbon monoxide. Average FTP carbon monoxide for vehicles characterized by idle carbon monoxide below 1 percent is 10.3 gm/mi; whereas the average for those above 1 percent idle carbon monoxide is 36.0 gm/mi.

Of 73 tests with more than 1 percent idle CO, only 9 (12 percent) were less than 15 gm/mi FTP CO. Of 54 tests with 1 percent or less idle CO, only 9 (17 percent) were greater than 15 gm/mi FTP CO, in spite of factors such as choke operation that are not related to warm engine idle CO, but can affect CO mass emissions.

Idle CO values obtained in this study are in close agreement with data collected by the Department on a statewide basis. Tests on over 400 1975 catalyst cars at various locations showed that the percentage of Chrysler, General Motors, and Ford vehicles with less than 1 percent idle CO were 20 percent, 60 percent, and 80 percent respectively. The data collected in this study gives corresponding values of 27 percent, 50 percent, and 72 percent respectively, suggesting that the results obtained on this small group of cars is a fair indication of what catalyst cars are doing in general.

TABLE 9

Average Emission Results; All Tests, All Manufacturers

Classification of Tests	No. Tests	No. Cars	Idle CO%	FTP				1 Hr 50 mph Cruise				CFS			
				HC	gm/ml CO	NO _x	HC	gm/ml CO	NO _x	mg/50% CO	HC	gm/ml CO	mg/50% CO	NO _x	mg/50% CO
All	127	49	2.4	1.7	25.1	2.9	0.1	0.8	2.4	4.1	0.5	6.2	2.8	2.7	
FTP CO < 15 gm/ml	53	23	0.4	0.9	7.6	3.2	0.1	0.3	2.5	5.1	0.2	1.6	3.1	4.9	
FTP CO < 15 gm/ml, HC < 1.5 gm/ml	49	22	0.3	0.8	7.1	3.2	<0.1	0.1	2.6	5.4	0.2	1.4	3.1	5.2	
FTP CO < 15 gm/ml, HC < 1.5 gm/ml, NO _x < 3.1 gm/ml	30	15	0.4	0.7	7.5	2.5	0.1	<0.1	1.9	5.7	0.1	1.3	2.5	5.8	
Idle CO ≤ 1%	54	26	0.2	0.9	10.3	3.0	0.1	0.7	2.5	5.1	0.2	1.8	3.0	5.1	
Idle CO > 1%	73	34	4.1	2.3	36.0	2.7	0.1	0.8	2.2	3.3	0.7	9.5	2.7	0.9	
FTP CO > 45 gm/ml	24	11	5.5	3.4	62.0	2.7	0.2	1.0	2.6	3.3	1.2	16.5	3.1	0.5	
Stall in Bag I of FTP	28	21	2.2	1.4	20.1	2.5	<0.1	0.5	2.1	6.3	0.3	5.0	2.5	3.7	
Fleet vehicles	76	25	2.7	2.0	36.1	2.6	0.1	0.8	2.1	4.0	0.5	7.2	2.6	2.0	
Private Vehicles	46	24	2.3	1.4	17.1	3.3	0.1	0.7	2.9	3.9	0.4	5.3	3.2	2.9	

TABLE 10
Average Emission Results; General Motors Vehicle Tests Only

Classification of Tests	No. Tests	No. Cars	Idle CO%	FTP			1 Hr 50 mph Cruise			CFS		
				HC	CO	gm/ml NO _x	HC	CO	gm/ml NO _x	mg/ml SO ₂	HC	CO
All General Motors Vehicles	50	18	1.8	1.3	16.4	3.0	<0.1	0.9	2.5	1.4	0.4	5.7
FTP CO < 15 gm/ml	29	11	0.3	0.9	7.1	3.1	<0.1	0.1	2.5	2.0	0.2	2.0
FTP CO < 15 gm/ml, HC < 1.5 gm/ml	28	11	0.3	0.7	7.0	3.1	<0.1	<0.1	2.5	2.0	0.1	0.2
FTP CO < 15 gm/ml, HC < 1.5 gm/ml, NO _x < 3.1 gm/ml	20	8	0.4	0.7	7.4	2.5	<0.1	<0.1	1.9	2.2	0.1	1.8
Idle CO ≤ 1%	25	9	0.1	0.9	6.3	3.2	<0.1	0.1	2.7	2.3	0.2	1.7
Idle CO > 1%	25	11	3.6	1.8	26.6	2.8	0.1	1.7	2.4	0.5	0.5	9.8
FTP CO > 45 gm/ml	3	2	3.8	4.1	58.7	3.1	0.2	5.0	2.6	0.2	1.3	27.8
SET-7 SO ₂ > 10 mg/ml	2	1	0.0	0.6	5.7	2.2	<0.1	<0.1	1.3	7.7	0.1	0.2
Fleet Vehicles	19	4	1.1	1.3	14.1	2.7	0.2	1.5	2.2	0.9	0.4	6.1
Private Vehicles	26	13	2.8	1.5	20.2	3.4	<0.1	0.6	2.9	0.9	0.4	6.5

TABLE 11
Average Emission Results; Ford Vehicle Tests Only

Classification of Tests	No. Tests	No. Cars	Idle CO%	FTP				1 Hr 50 mph Cruise				CFS			
				HC	CO	gm/ml	NO _x	HC	CO	gm/ml	NO _x	HC	CO	gm/ml	mg/ml SO _x
All Ford Vehicles	18	9	0.7	1.0	11.5	3.2	3.2	0.3	2.2	2.8	8.7	0.4	3.9	3.3	8.5
FTP CO < 15 gm/ml	12	6	0.2	0.9	5.3	3.8	3.8	0.3	0.9	3.4	10.3	0.4	1.2	3.9	11.7
FTP CO < 15 gm/ml, HC < 1.5 gm/ml	11	6	0.2	0.8	4.4	3.7	3.7	0.2	0.3	3.4	11.1	0.3	0.8	3.9	12.5
FTP CO < 15 gm/ml, HC < 1.5 gm/ml, NO _x < 3.1 gm/ml	3	2	0.0	0.6	2.4	2.7	2.7	0.2	0.1	1.7	15.7	0.2	0.1	2.8	22.1
Idle CO ≤ 1%	13	6	0.2	0.9	9.2	3.3	3.3	0.2	2.5	3.0	9.4	0.3	3.3	3.5	10.2
Idle CO > 1%	5	3	2.1	1.3	17.5	2.9	2.9	0.4	1.6	2.4	7.1	0.5	5.5	2.4	4.1
FTP CO > 45 gm/ml	0	0	---	---	---	---	---	---	---	---	---	---	---	---	---
SET-7 SO _x > 10 mg/ml	6	4	0.0	0.6	2.8	3.6	3.6	0.2	0.0	3.2	14.5	0.2	0.3	3.9	17.2
Fleet Vehicles	5	2	0.3	0.8	16.5	2.4	2.4	0.1	4.3	1.4	7.1	0.2	6.2	2.2	7.5
Private Vehicles	13	7	0.8	1.0	9.5	3.5	3.5	0.3	1.4	3.3	9.4	0.4	3.0	3.7	8.9

TABLE 12
Average Emission Results: Chrysler Vehicle Tests Only

Classification of Tests	No. Tests	No. Cars	Idle CO%	FTP				1 Hr 50 mph Cruise				CFS			
				HC	CO	gm/mi	NO _x	HC	CO	gm/mi	NO _x	mg/mi	HC	CO	mg/mi
All Chrysler Vehicles	59	22	3.5	2.2	36.5	2.6	2.6	0.1	0.2	2.1	4.9	0.6	7.3	2.6	1.9
FTP CO < 15 gm/mi	12	6	0.9	1.0	11.1	2.8	<0.1	<0.1	<0.1	1.7	7.5	0.2	1.2	2.3	4.2
FTP CO < 15 gm/mi, HC < 1.5 gm/mi	10	5	0.5	0.9	10.5	2.8	<0.1	<0.1	<0.1	1.8	8.7	0.1	0.4	2.4	4.9
FTP CO < 15 gm/mi, HC < 1.5 gm/mi, NO _x < 3.1 gm/mi	7	5	0.6	0.9	10.3	2.5	<0.1	<0.1	<0.1	1.9	11.3	<0.1	0.5	2.4	6.3
Idle CO ≤ 1%	16	11	0.3	1.1	17.6	2.6	<0.1	<0.1	0.1	2.0	6.0	0.1	0.8	2.5	4.7
Idle CO > 1%	43	20	4.7	2.6	43.6	2.7	0.1	0.2	2.1	4.4	0.8	9.8	2.7	0.8	
FTP CO > 45 gm/mi	21	9	5.7	3.3	62.5	2.7	0.2	0.4	2.6	3.7	1.2	14.9	3.1	0.6	
SET-7 SO _x > 10 mg/mi	4	4	0.1	1.2	16.1	2.3	0.1	<0.1	2.0	11.4	0.1	0.2	2.2	13.0	
Fleet Vehicles	52	18	3.6	2.3	38.8	2.6	0.1	0.2	2.1	4.9	0.6	7.7	2.6	2.0	
Private Vehicles	7	4	3.1	1.4	19.8	2.8	0.1	<0.1	1.7	5.0	0.4	4.4	2.5	0.9	
Police Cruisers	14	2	4.4	3.0	53.8	3.0	0.0	0.0	3.2	2.0	0.6	13.7	3.8	0.8	
Fleet -- No Police Cars	38	16	3.2	2.1	33.2	2.4	0.1	0.3	1.7	5.9	0.6	5.5	2.2	2.4	
Fleet and Private Vehicles -- No Police Cars	45	20	3.2	2.5	31.1	2.5	0.1	0.2	1.7	5.8	0.6	5.4	2.2	2.2	

Vehicles stalled at the beginning of the FTP in 28 tests. In spite of the restart (by Federal Register procedures), average regulated emissions for these tests are lower than overall average idle carbon monoxide is 2.2 percent for these tests, also less than overall average value.

Tests on fleet-operated vehicles show considerably higher FTP carbon monoxide emissions than do tests on privately-owned vehicles. Any comparison of fleet and private vehicles must be made with care, however, because the manufacturer-mix differs for the two groups (Table 8) and because the fleet vehicles have much higher mileage accumulations.

b. Sulfate Emissions

Sulfate emissions for 127 tests average 2.7 mg sulfate (SO_4) per mile. For tests with less than 15 gm/mi FTP carbon monoxide, cease to 5.8 mg/mi in tests where HC, carbon monoxide, and NO_x standards are met. Grouping sulfate emissions data according to vehicles' idle carbon monoxide value also reveals a correlation. Fifty-four tests on vehicles having less than 1 percent idle carbon monoxide yield an average of 5.1 mg/mi SO_4 , and 73 tests with greater than 1 percent idle carbon monoxide give an average of 0.9 mg/mi SO_4 . In 12 tests, sulfate emissions are over 10 mg/mi; in each case the idle CO is 0.0 percent.

Significant variation in results are observed when the data are grouped by manufacturer (Tables 10-12). The effect of air pumps on Ford vehicles is seen in the low carbon monoxide and relatively higher sulfate emissions. Frequent rich carburetion encountered in Chrysler products corresponds to the high carbon monoxide and low sulfate emissions observed.

In order to determine the sulfate emissions at idle, two filters are collected during idle periods of the test sequence (see Table 7); one is collected during the 5-minute idle separating the 50 mph cruise from the first CFS, and a second is a composite sample from the idle periods after CFS cycles three, four, and five. These filters are analyzed for soluble sulfate on the BCA apparatus. These data show idle sulfate emissions to be very low. Combining the driving cycle and the following idle period, less than 2 percent of the sulfate collected and 0.2 percent of the fuel sulfur recovery is from the idle period.

c. Sulfur Dioxide Emissions

Two distinct types of sulfur dioxide (SO_2) emissions have been quantified. One type is typified by high idle carbon monoxide values; the other, by low idle carbon monoxide emissions. Figure 7 shows both types of sulfur dioxide emissions for the same car in two successive tests.

The two types are observed when a car is decelerated to idle. The first type, which shows insignificant sulfur dioxide emissions in any of the 5-minute idle periods, occurs on vehicles with low idle carbon monoxide values typical of proper carburetion. The second sulfur dioxide emission pattern, which is characterized by a short burst of sulfur dioxide upon deceleration, either at the end of the 50 mph cruise or at the end of the CFS cycles, occurs in vehicles which have high carbon monoxide values. A strong sulfur odor is readily noticed in this case.

In order to quantify this spike phenomenon, the sulfur dioxide concentration is integrated separately during each driving cycle and idle period, yielding a sulfur dioxide mass value for each. For comparison purposes, a ratio of these masses is defined as follows:

$$\text{SO}_2 \text{ purge fraction} = \frac{\text{Spike SO}_2 \text{ mass}}{\text{Cycle SO}_2 \text{ mass} + \text{spike SO}_2 \text{ mass}}$$

A purge fraction of 1.0 thus corresponds to a situation where the total SO_2 emitted from a particular driving cycle (i.e., 1-hr, 50 mph cruise or CFS cycle) is attributable only to the idle segment. Table 13 gives average purge fraction values for the four catalyst configurations for both the post 50 mph cruise idle and for the post CFS idle. CFS values reported are the average of purge fractions for cycles 3, 4, and 5. For all system configuration, it is found that, within a given test, there is reasonable consistency of purge fractions for all five CFS cycles. SO_2 purge fraction for the 50 mph cruise, classified by idle CO emissions, is shown in Figure 8. The greater SO_2 purge fraction from tests with 1 percent or less idle CO than for those with greater than 1 percent idle CO is readily apparent.

4. Effect of Mileage Accumulation

Table 14 shows average FTP regulated emissions for various mileage ranges by manufacturer. Data from tests on vehicles with over 30,000 miles are predominantly from fleet vehicles with high mileage accumulation rates.

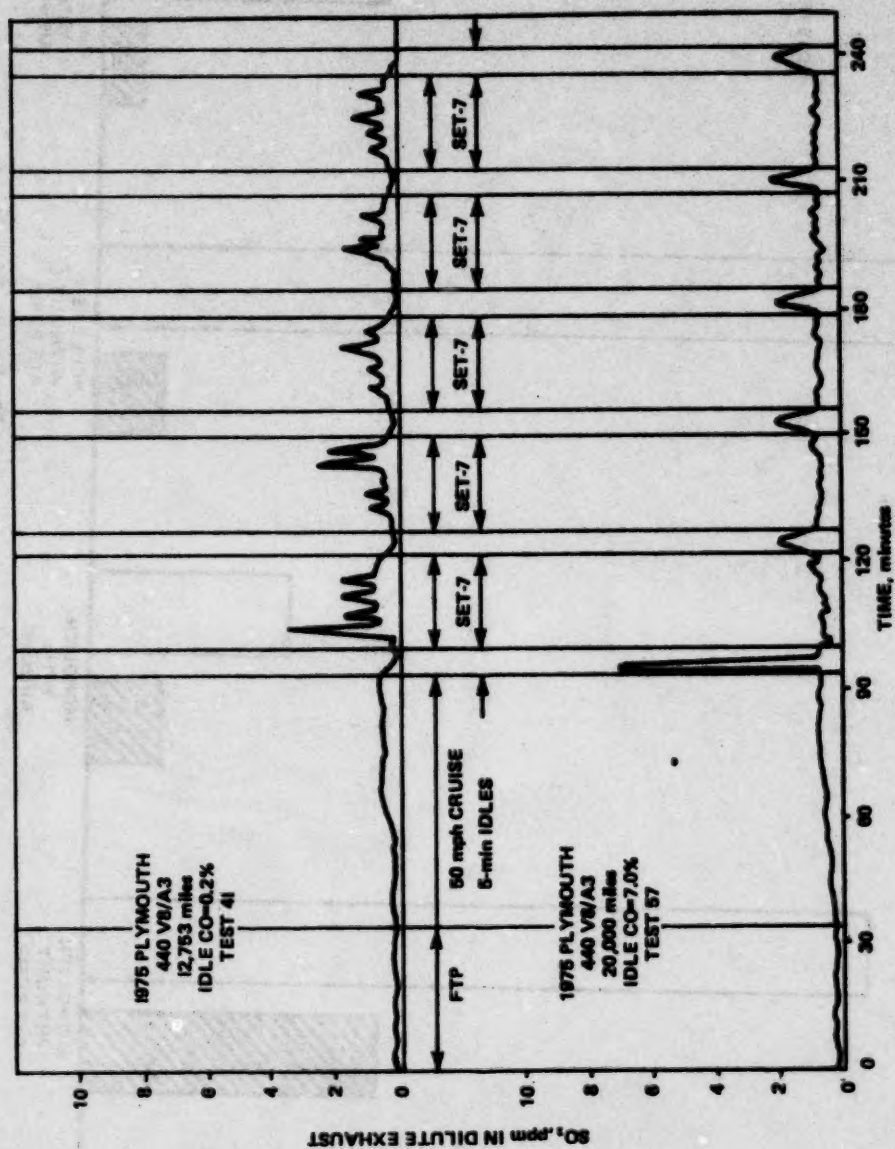


Figure 7. Two distinct patterns of sulfur dioxide emissions, high and low idle.

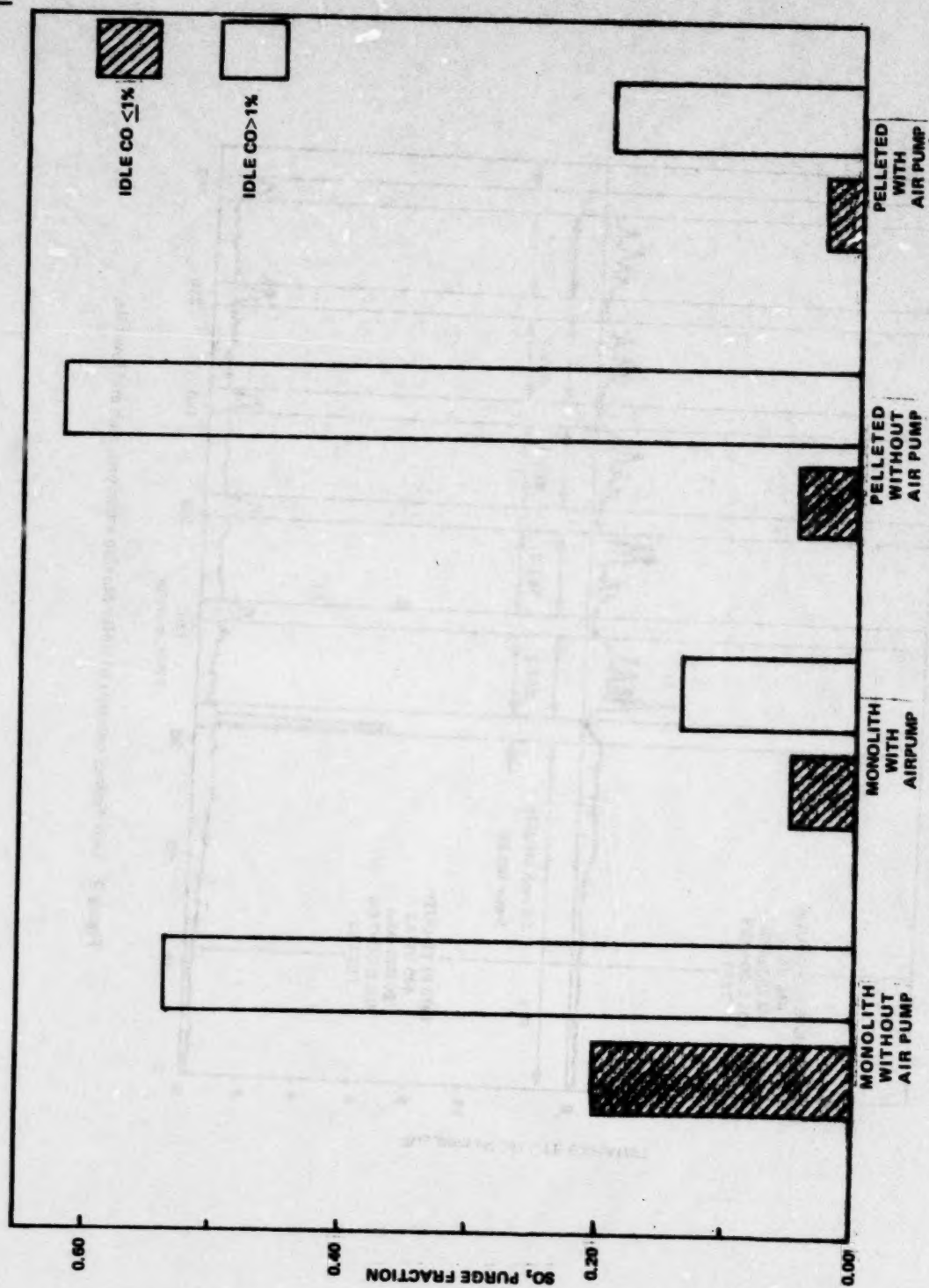


Figure 8. Sulfur dioxide purge fractions, post 50 mph cruise idle.

TABLE 13

Sulfur Dioxide Purge Fractions

<u>Configuration</u>	<u>50 MPH Cruise</u>	<u>CFS</u>
(1) Monolith without Air Pump (M)	0.46	0.25
(2) Monolith with Air Pump (MA)	0.12	0.10
(3) Beaded with Air Pump (B)	0.45	0.32
(4) Beaded with Air Pump (BA)	0.06	0.16

TABLE 14

Average Emissions; Mileage Accumulations
(gm/mi)

Mileage Interval (Thousands)	All Tests					GM Tests					Ford Tests					Chrysler Tests							
	No. Tests		HC	CO	NO _x	No. Tests		Cars	HC	CO	NO _x	No. Tests		Cars	HC	CO	NO _x	No. Tests		Cars	HC	CO	NO _x
0-5	20	16	1.1	16.6	2.8	7	6	0.9	12.0	2.5	7	5	1.1	8.0	3.6	6	6	1.4	32.0	2.3			
5-10	22	20	1.5	24.8	2.7	7	7	1.2	20.2	2.4	4	4	0.8	5.0	3.6	11	10	2.1	34.9	2.6			
10-15	26	25	1.5	20.6	2.7	9	8	1.0	12.0	2.7	3	3	0.7	7.2	4.0	14	14	2.0	28.9	2.4			
15-20	15	15	2.2	29.3	2.8	8	8	1.7	22.7	3.0	1	1	1.2	21.1	2.1	6	6	3.1	39.5	2.6			
20-30	31	24	1.9	28.9	2.9	12	9	2.0	19.9	3.4	2	2	1.1	28.9	1.6	17	13	1.9	35.3	2.6			
30-40	10	7	2.1	34.3	3.9	5	4	0.8	10.1	4.3	1	1	1.1	30.4	1.3	4	2	3.9	65.4	4.0			
40-50	3	3	2.1	31.5	3.5	2	2	0.9	9.0	3.3	---	---	---	---	---	1	1	4.6	76.4	4.0			

Considering all tests, HC emissions rise from 1.1 gm/mi in the 0-5,000 mile interval to a fairly constant value of approximately 2.0 gm/mi after 20,000 miles. The manufacturer breakdowns show generally higher HC emissions from Chrysler products than from Ford or General Motors. Carbon monoxide emissions exhibit a slightly irregular but definitely increasing trend with mileage. In the 0-5,000 mile interval, the carbon monoxide emissions for Chrysler products are already higher than for either General Motors or Ford vehicles, and the subsequent increase with mileage is readily apparent. The apparent reduction in General Motors carbon monoxide emissions after 20,000 miles reflects the preponderance of high mileage fleet vehicle tests in the data for over 20,000 miles. Among GM products tested, fleet cars have lower FTP emissions than private vehicles. More Ford tests in all intervals are needed to determine the significance of the indicated trend of increasing carbon monoxide emissions with mileage. In contrast to GM tests, Chrysler fleet vehicles exhibit higher emissions than do the few Chrysler private vehicles (Table 12).

Sulfur dioxide purge behavior has not been found to be a function of vehicle mileage. Detailed emissions results for two vehicles over extended mileage periods are shown in Tables 15-16. In Table 15, the AEL control car consistently shows both low regulated emission and low sulfur dioxide purge fraction for five tests spanning nearly 14,000 miles. Through 3 tests (12,753 miles), a police cruiser exhibits similar behavior (Table 16). At 12,753 miles, idle carbon monoxide, FTP carbon monoxide, and the 50 mph idle purge fraction are 0.2 percent, 15.89 gm/mi, and 0.05 respectively. At the 20,200 mile test, however, idle carbon monoxide, FTP carbon monoxide, and 50 mph purge fraction have all greatly increase to 7.0 percent, 80.72 gm/mi, and 0.4 respectively. The change in SO_2 emission pattern between these two tests is graphically illustrated in Figure 8.

Although one object of this study is to determine the effect of vehicle mileage on sulfate emissions, no overall correlation is apparent at this time. High idle carbon monoxide, deactivated catalysts, low fuel sulfur levels, and the absence of an air pump combine to yield low sulfate values that do not correlate with vehicle miles.

5. Conclusions

Testing of in-use catalyst vehicles has shown:

- a. Low sulfate emissions of 1.3 mg/mi for cars without air pumps and 4.9 mg/mi for air pump cars as tested by stabilized CFS driving. These values were obtained from fuel with an average of 0.017 weight percent sulfur.
- b. High CO emissions by FTP testing and idle measurements.
- c. Purge of large amounts of SO_2 from catalysts upon deceleration to idle when idle CO is high.

TABLE 15

Summary of Test Results for Car 1

Test No.	17	31	56	87	124
Mileage	2,715	4,982	8,319	10,317	13,732
<u>Idle Data</u>					
CO(%)	0.0	0.0	0.0	0.0	0.0
HC(ppm)	90.	70.	90.	70.	40.
<u>Regulated Emissions</u> (g/mi)					
HC	0.59	0.57	0.56	0.70	0.63
CO	6.19	5.21	6.27	4.96	7.85
NO _x	2.35	2.16	2.21	2.62	2.36
<u>SO₂ Production</u> (mg/mi)					
FTP	0.06	1.64	0.72	0.71	0.70
50 mph	3.33	6.53	8.24	7.06	5.26
SET-7, Cycle 1	6.57	13.37	12.40	5.15	7.43
SET-7, Cycle 2	7.46	13.38	12.23	3.66	7.37
SET-7, Cycle 3	9.96	16.79	15.52	4.55	5.22
SET-7, Cycle 4	9.92	18.08	13.93	7.66	6.36
SET-7, Cycle 5	9.31	16.40	14.88	5.86	7.56
<u>SO₂ Purge Fraction</u>					
50 mph	0.04	0.02	0.01	0.05	0.02
SET-7	0.06	0.07	0.04	0.03	0.03
<u>Sulfur Balance</u> (% Recovery)					
FTP	4.7	17.0	1.0	0.7	1.6
50 mph	18.0	39.7	17.2	11.7	13.7
SET-7	51.6	61.1	37.7	36.6	36.5
<u>Fuel S(wt. %)</u>					
	0.017	0.019	0.021	0.018	0.018

TABLE 16

Summary of Test Results for Car 3

Test No.	6	30	41	57	94	110
Mileage	17	9,298	12,753	20,200	30,288	35,226
Idle Data						
CO (%)	0.1	0.0	0.2	7.0	7.0	5.8
HC (ppm)	50.	125.	400.	460.	460.	400.
Regulated Emissions (g/mi)						
HC	0.99	0.76	1.03	3.18	3.40	3.61
CO	14.32	7.74	15.89	80.72	90.69	66.98
NO _x	2.98	2.35	2.11	2.14	2.38	3.95
SO ₂ Production (mg/mi)						
FTP	0.59	1.24	0.44	0.23	1.66	0.55
50 mph	3.33	2.92	1.19	1.12	3.44	3.20
SET-7, Cycle 1	1.97	3.62	0.78	0.10	1.00	0.49
SET-7, Cycle 2	1.64	3.73	0.87	0.18	0.49	0.42
SET-7, Cycle 3	2.40	3.83	0.81	0.13	0.56	0.47
SET-7, Cycle 4	2.41	3.83	0.85	0.22	0.52	0.49
SET-7, Cycle 5	2.96	4.31	0.76	0.13	0.47	0.49
SO ₂ Purge Fraction						
50 mph	0.17	0.07	0.05	0.40	0.33	0.30
SET-7	0.06	0.08	0.03	0.23	0.24	0.22
Sulfur Balance (% Recovery)						
FTP	5.2	10.3	9.5	2.7	2.5	2.8
50 mph	41.2	42.8	29.4	22.8	22.6	27.4
SET-7	91.0	89.2	75.3	39.6	36.7	57.1
Fuel S (wt.%)	0.016	0.012	0.010	0.012	0.012	0.012

d. Little particulate sulfate in idle periods for either high or low CO conditions.

e. Marked variation in emission pattern by vehicle manufacturer.

f. Frequent enrichment of idle mixture settings.

D. Vegetation Studies

Investigators at the Department of Plant Pathology at the University of Minnesota, St. Paul, Minnesota, are studying the effects of sulfuric acid aerosol on vegetation under a grant from EPA.

A greenhouse facility has been developed to expose vegetation to submicrometer sulfuric acid aerosol. The exposure system consists of a bank of six clear acrylic tubes (30.5 cm diameter x 1.2 m length) lined with clear teflon film (0.01 mm thick). Two of the six tubes provide the sulfuric acid aerosol and the remaining four serve as controls. All the tubes are provided with teflon inlet ports through which parts or whole plant shoot systems can be inserted for the exposure. The design facilitates simultaneous exposure of comparable parts of the same plant to both the acid aerosol and the control environments, thus providing an efficient system for studying acute effects.

The sulfuric acid aerosol is generated by nebulizing concentrated sulfuric acid, followed by inertial removal of particles larger than $1\text{ }\mu\text{m}$ and charge neutralization of the submicrometer particles. Mass flow calculations during the initial experiments indicate a sulfuric acid aerosol concentration of $25\text{--}30\text{ mg/m}^3$. Preliminary cascade impactor studies show that more than 50 percent of the particulate mass is less than $0.5\text{ }\mu\text{m}$ in diameter and that 30 percent of the particles are below the limits of inertial impaction at atmospheric pressure.

Hybrid poplar, pinto bean, and soybean when exposed to $25\text{--}30\text{ mg/m}^3$ sulfuric acid aerosol for 4 hours showed marginal and tip necrosis. This symptom is very similar to fluoride- and chloride-induced injury on broad-leaved plants.

Additional work is planned to further characterize the aerosol, to screen a variety of plant species for their response to the aerosol under different environmental conditions, and to determine the aerosol neutralization characteristics of NH_3 in relation to plant effects.

IV. PROBLEM AREAS

A. Ultrafine Sulfuric Acid Studies

Automobiles equipped with current catalytic converters emit ultrafine sulfuric acid (H_2SO_4) mist. Animal exposure studies using particles larger than ultrafine range ($< 0.1 \mu\text{m}$ mass median diameter) show that as the particle size diminishes toward ultrafine, the pulmonary resistance increases in exposed lungs. The EPA needs data on the effects of ultrafine H_2SO_4 mist on the lung to compare with the large particulate data. There have been problems in the generation and calibration of the ultrafine aerosol and in the development of analytic techniques for animal exposures. These problems are now near solution, and exposure studies will begin soon.

B. Nitrogen Dioxide

The effects of nitrogen dioxide (NO_2) on human health have become of increasing importance at a rate which has overtaken the capability of HERL facilities to study them. Because of the new priority, the inadequate NO_2 investigation facilities at HERL must be expanded to allow more sophisticated human exposure studies.

C. Manganese Exhaust Products

There has been some question regarding what compounds result from combustion of automotive fuel containing manganese. Until these questions are reached, experiments in health effects of inhalation of manganese compounds cannot be evaluated in terms of relevance to exposure to automotive exhaust containing manganese combustion products.

D. Diesel Exhaust

As the number of diesel-equipped vehicles grows, so does the concern for the resulting increased diesel emissions and the associated risks to health. EPA is confronted with serious problems encompassing the generation of appropriate diesel-emission samples, calibration of the equipment, and isolation of the components of the extremely complex exhaust to determine the effects of the single pollutants. The vast number of components comprising the total complex diesel exhaust must each be isolated to identify it with effects observed in exposure studies. Potentiation from interaction of these components can then be separated from the cause-effect relationship of the single pollutants. This problem will require close coordination with the engineering effort and advances in state-of-the-art analytical technology.

V. PLANS FOR FUTURE RESEARCH

A. Animal Studies

1. Sulfates

The objective of a study initiated in the fall of 1976 is to determine how metallic sulfates, sulfur dioxide, and sulfuric acid can alter respiratory defense mechanisms, particularly the alveolar macrophage. This work is being conducted under EPA grant to the School of Public Health, Harvard University. Since the grant was not initiated until October 1976, only preliminary experiments have been conducted.

Immunosuppressive effects of metal sulfates will be the focus of new studies undertaken by HERL at Research Triangle Park, N.C. These planned experiments will be in-house.

The catalytic converters currently used in vehicles have been shown to generate or allow sulfuric acid (H_2SO_4) emissions in the form of ultrafine particulate. It has been shown that H_2SO_4 aerosols in larger range particulate size produce harmful effects on animals. It has been difficult, however, to measure the health effects of H_2SO_4 in the ultrafine ($< .1 \mu m$ mass median diameter) range. Animal exposure experiments have been designed to determine how the health effects of ultrafine aerosol differ from the effects of aged aerosols. It has been difficult to measure levels of ultrafine H_2SO_4 generated under laboratory conditions during attempts to simulate "real-world" conditions, but recent designs have produced equipment to overcome this barrier.

2. Metals

No new platinum studies are planned, and most extramural projects have been completed or are nearing completion. Research for the ongoing studies will continue with final reports due in 1977 or 1978. Studies (discussed in Section III) for which final reports are shortly expected are the following:

a. An investigation of whether a hypersensitive state can be induced by exposure to platinum or to palladium metal.

b. An investigation of the use of leucocyte metabolism as an indicator of health effects.

c. A study of the biological activity of platinum in the induction of pulmonary neoplasia by benzo(a)pyrene and of the role of platinum in changes of transpulmonary absorption, pulmonary clearance, and pulmonary response to intrapulmonary particulates.

d. An evaluation of the effects of platinum sulfate in major metabolic pathways in the central nervous system.

e. Chemical characterization of one MePt compound prepared from K_2PtCl_6 and methylcobalamin (MeB_{12}) and isolation and characterization MePt products from the reaction of $Pt(SO_4)_2$ with MeB_{12} .

f. Studies of the cellular toxicity and mutagenicity of at least one MePt compound as well as several related Pt-salt complexes.

g. Evaluation of analytical methods for measuring trace elements in biological matrices (especially mammalian tissue). A series of reports will document the various limits of detection achieved; concentration, separation, and extraction techniques; sources of contamination; and other considerations in order to recommend the most promising of the methods developed applied, and reported to date. It is anticipated that this series of reports on methods for individual metals (platinum, palladium, nickel, manganese, chromium, cerium, and vanadium) will be valuable to researchers in the area of trace metals, especially where measurements of extremely small amounts of metal in tissue samples are necessary for interpretation of experimental results.

h. The HERL at Research Triangle Park plans to do further work on determining the effects of manganese oxides alone and in combination with sulfuric acid on animal tissues.

In addition to these reports of separate studies, a followup report is planned for publication in late 1978 to complement the report of the 1975 review conference on platinum research which was published in 1976 as "Proceedings - Catalyst Research Program Platinum Research Review Conference." Since platinum had received little attention in research prior to the establishment of the CRP, this summary report should become an extremely useful reference for future researchers in the field.

B. Human Studies

A project scheduled to begin in early 1977 will investigate the potential health effects of low-level sulfuric acid aerosols in a concentration range of 50 to 200 $\mu g/m^3$ with a mass median diameter (MMD) particle size in the range of 0.05 to 0.5 micrometers. It is hoped that this range will lead to information valuable in light of the increased use of the catalytic converter which produces a sulfuric acid aerosol. Previous relevant studies and the methodology adopted for this project receive detailed discussion in Section IIIB.

If there is found to be an observable effect from sulfuric acid mist on the health parameters designated for the study, further studies will be initiated to aid in the development of a regulatory standard. If there is no observable effect, studies in higher risk groups, i.e., those with chronic lung disease, may need to be performed.

Power plant emissions and automobile exhaust contain nitrogen oxides (NO_x) which are in themselves irritants or decompose and react with other components to form aerosol pollutants. Research Triangle Park has plans for studies of short-term human exposures to the oxides of nitrogen in 1977.

C. Mobile Source Emissions

The research project engaged in the measurement of sulfate, particulate, and regulated emissions for a group of 49 in-use catalyst vehicles will continue through 1977. See Section IIIC for a report on the current status of the project.

HERL at Research Triangle Park, N.C., is initiating studies using surrogate diesel particulate emissions to investigate effects on health. Bioassays will include in vitro screening tests for mutagenicity resulting from exposure to diesel whole exhaust and to its isolated components.

The final HERL report on in-use catalyst-equipped vehicles is to be completed in FY 78.

D. Vegetation Studies

Additional work is planned by the Department of Plant Pathology University of Minnesota, to further characterize sulfuric acid aerosol, to screen a variety of plant species for their response to the aerosol under different environmental conditions, and to determine the aerosol neutralization characteristics of NH_3 in relation to plant effects.

VI. CONCLUSIONS

Although many projects performed by the Health Effects Research Laboratory at Research Triangle Park, N.C., are continuing studies for which final results are not yet available, several conclusions are indicated at this time.

Laboratory animals exposed to sulfuric acid aerosol for short periods of time experienced a decrease in hematocrit, a greater increase in the number and percent of polymorphonuclear leucocytes (PMN) than air-exposed

animals, and a greater decrease in the number and percent of lymphocytes than controls. Exposure to ozone immediately before exposure to sulfuric acid resulted in an increase in respiratory infections as compared to animals exposed only to one pollutant or to both pollutants in reverse order. Plants exposed to sulfuric acid showed marginal and tip necrosis similar to fluoride- and chloride-induced injury on broadleaved plants.

Results of metals studies indicated that manganese inhalation enhances respiratory infections; that platinum does not induce allergy, but that palladium, when complexed with albumin, does induce a delayed allergy; and that platinum sulfate is a severe eye irritant, may have some cytogenetic activity, and appears to have a mildly depressive effect on behavior. It has also been shown that platinum, as platinum sulfate or as potassium hexachloroplatinate, can be methylated in the same way that mercury can be methylated.

Several conclusions can be drawn from the studies on mobile source emissions. Tests on 49 in-use catalyst vehicles show, in general, low sulfate emissions and high carbon monoxide values. Few cars tested have met all 3 emissions standards (15.00 gm/mi CO, 3.1 gm/mi NO, and 1.5 gm/mi HC); the carbon monoxide regulation was exceeded most often. A direct correspondence exists between high idle carbon monoxide and carbon monoxide mass emissions, and carbon monoxide emissions are inversely related to sulfate emissions. In addition, the use of an air pump leads to low carbon monoxide but to higher sulfate emissions. It has also been found that large amounts of sulfur dioxide are purged from catalysts upon deceleration to idle when idle carbon monoxide is high. The emissions were found to vary significantly according to manufacturer. Many cars revealed enrichment of the idle mixture settings. In relation to mileage, the tests indicate that HC emissions rise with mileage to a fairly constant value of 2.0 gm/mi after 20,000 miles and that carbon monoxide emissions show a slightly irregular but definitely increasing trend with mileage. Sulfur dioxide purge behavior has not been found to be a function of mileage, however, and no correlation between mileage and sulfate emission is apparent at this time.

APPENDIX D-1

AEROSOL GENERATION AND MONITORING, HUMAN EXPOSURE

The basic design of the 2.4 x 2.4 x 2.2 meter acrylic plastic controlled exposure laboratory which was designed for use with pollutant gases has been modified for use with H_2SO_4 aerosol.

The air inlet system has been modified to include particulate and gas (CBR) filter elements. Preconditioned building air will be drawn through these filters to insure that the test subject is exposed only to the pollutants defined by the test protocol. The H_2SO_4 aerosol is added to the clean air inlet after the filters and upstream from the mixing and chamber inlet distribution elements. These elements are designed for minimal effects on aerosol particle size and concentration while insuring a uniform distribution of aerosol concentration in the human exposure zone of the chambers.

A block diagram of the present exposure chamber system with the CBR filter units added to the supply and exhaust air subsystem is provided by Figure 9. The input filter unit occupies a volume of approximately 24 cubic feet near the entrance of the chamber air input supply duct. The chamber output filter is located outside the building near the chamber exhaust blower. The electrical output of the aerosol monitoring instruments is used to control the rate of aerosol generation. The aerosol generator, exposure chamber, aerosol monitors, and a pollutant flow controller form a closed loop control system similar to that presently used in the approved ozone exposure study. The response time of the aerosol monitors is less than the 90-second air exchange rate of the chamber.

The existing chamber safety system consisting of the alarm system and pollutant flow inhibitor blocks illustrated in Figure 10 will be expanded to include the aerosol generating system. Any abnormal conditions detected by the safety system will result in immediate shut down of the generators and an automatic purge of the pollutant in the chambers.

Sulfuric acid aerosol will be generated using the fuming sulfuric acid technique described by Scaringelli and Rehme (13). The particle diameter of these aerosols in 50 percent Rh air was found to be approximately 0.5 μm . In another animal exposure study described by Hinners, et al. (14) using this H_2SO_4 generation technique, the aerosol particle diameter was found to be approximately 1 μm . By adjustments to generator air flow rates and other factors affecting ozone nuclei growth patterns (dilution rates, dilutor design, generator temperature control, etc.), it is expected that the H_2SO_4 aerosol particle diameter can be controlled to approximately 0.05 to 0.5 μm with relative ease. The mass concentration will be controlled at $100 \mu g/m^3 \pm 25$ (measured by EAA) by adjustment of the dry air flow over the surface area of fuming sulfuric acid in the generator. Exposure atmospheres will be exhausted through high efficiency particulate filters to the outside of the building.

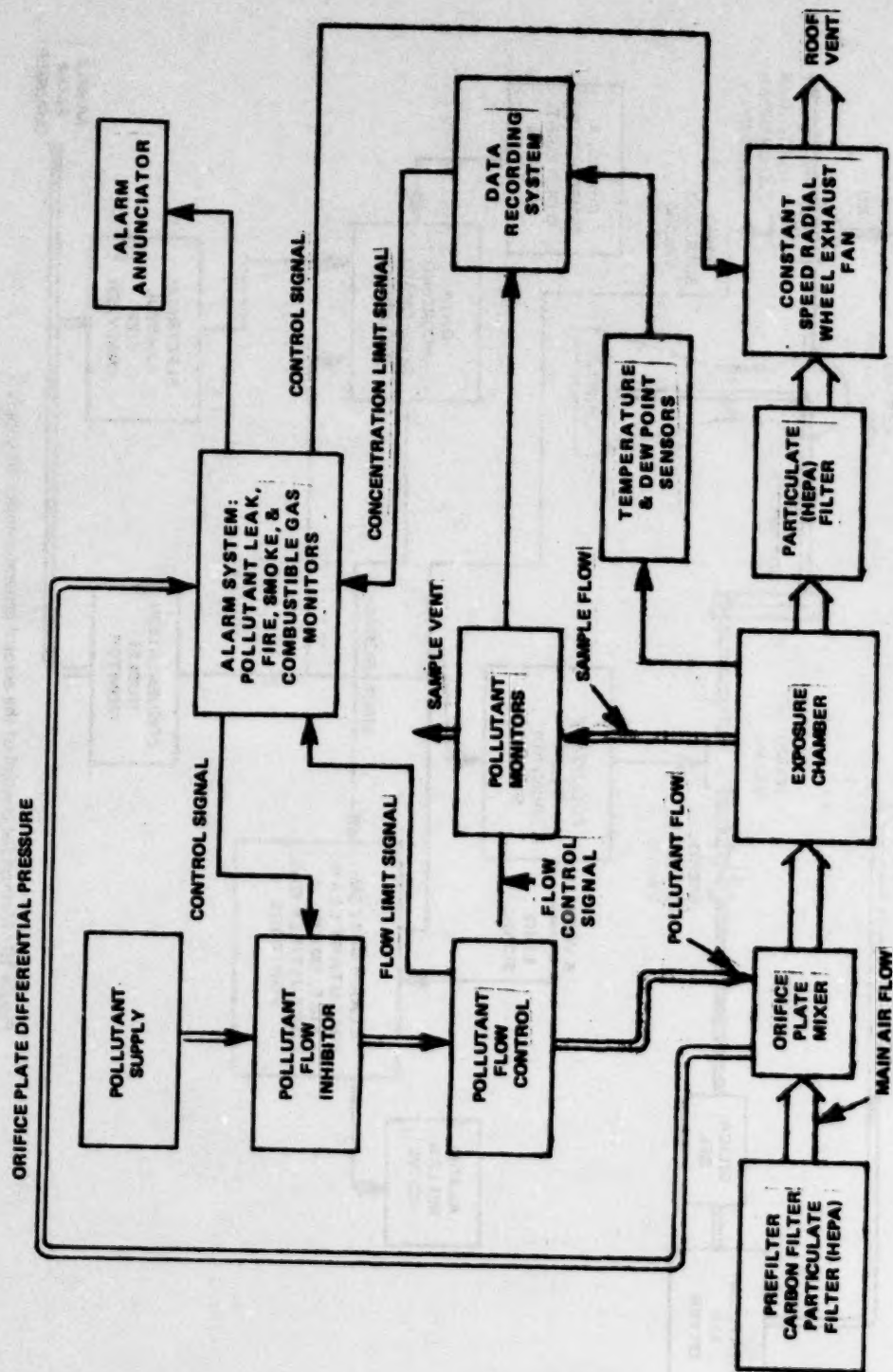


Figure 9. Exposure chamber system with added filter units.

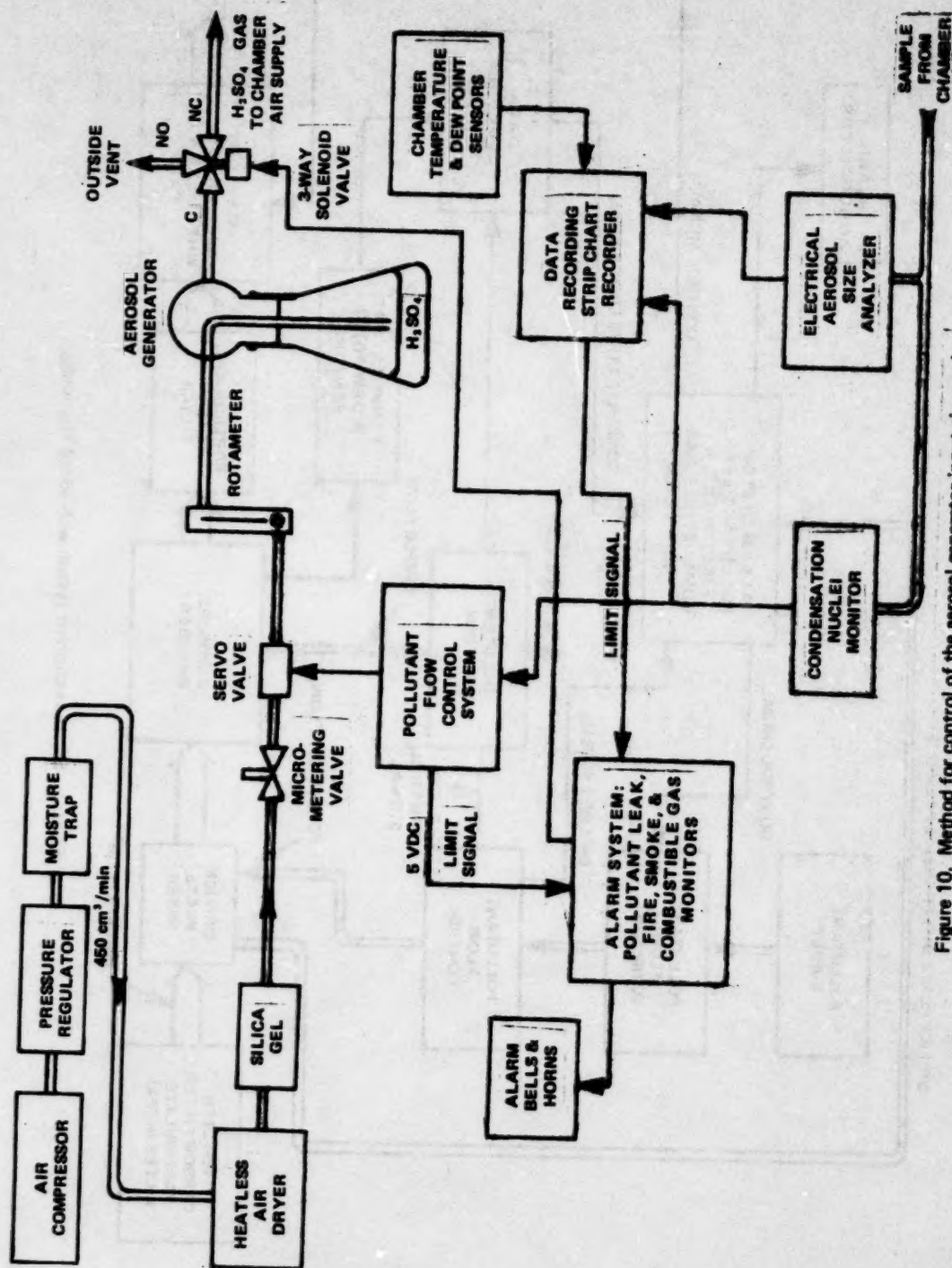


Figure 10. Method for control of the aerosol generator input air supply.

The methods for control of the aerosol generator input supply air will be similar to that presently used for the ozone generator. As shown in Figure 10, dry compressed air will flow through a system of pressure regulators, flow restrictor valves, a flow-controlling servo valve, and a rotameter to the input of the aerosol generator. The electrical outputs of the particle counter and aerosol analyzer will be used to operate a servo controlled valve or mass flow controller to maintain and adjust the volume of dry air through the aerosol generator for the desired concentration in the exposure chamber. A normally closed solenoid valve on the output line from the air supply will shut off the air supply to the aerosol generator whenever it becomes necessary to stop the flow of aerosol particulates. The maximum flow of pollutant into the chamber will be restricted by the micrometering valve and a limit position of the servo valve.

Aerosol particle size and mass concentration monitoring will be accomplished using several measurement instruments. Two instruments giving real-time instantaneous response will be used to monitor changes in aerosol size and number concentration. One of these instruments (condensation nuclei counter) measures the number of particles in the size range 0.001 μm to 1.0 μm diameter. The instrument (light-scatter particle counter) measures the size and number of aerosol particles individually, one-by-one in the size range of 0.3 μm to 6 μm diameter. These two instruments will be used by the control operator to adjust the aerosol generators to a steady output rate within preselected size and concentration limits. An additional instrument, the electric mobility aerosol analyzer (EAA), is the primary instrument to obtain average aerosol mass concentration and MMD exposure data over a size range of 0.0032 to 1.0 μm . This is a continuous, real-time instrument that counts particles according to size.

Because these proposed studies will be conducted in controlled environments where the exposure aerosol is generated from pure H_2SO_4 into a clean, particle-free atmosphere, monitoring instruments need not be specific for the chemical composition of the aerosol. However, the continuous monitoring instruments must accurately measure the exposure aerosol concentration and size. To insure this accuracy, standard manual calibration techniques will be employed.

Particle size calibration measurements will be periodically made microscopically from samples collected by thermal precipitation, inertial impact, and by filtration. Also, the light-scatter particle counter will be calibrated using aerosols generated from slurries of known particle sizes of polystyrene latex spheres. Mass concentration calibration measurements will be made by collecting samples on high efficiency filters and determining the mass of H_2SO_4 collected using standard chemical analysis methods (i.e., colorimetric and conductimetric).

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APPENDIX E

THIRD ANNUAL CATALYST RESEARCH PROGRAM REPORT

Prepared By

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I. INTRODUCTION

As hydrocarbon, carbon monoxide, and nitrogen oxide emissions are controlled, various unregulated emissions may be altered. Introduction of a new emission control system can increase or decrease the level of a particular unregulated pollutant or, in extreme cases, result in formation of entirely new pollutants. It is important that these pollutants be characterized to be certain that control of regulated emissions creates no problems in other areas.

The unregulated pollutants discussed in this section are sulfuric acid, hydrogen cyanide, ammonia, ruthenium, polynuclear aromatic hydrocarbons, and diesel particulate.

II. SULFURIC ACID

A. Introduction

The use of oxidation catalysts results in oxidation of both hydrocarbons and carbon monoxide. In addition, oxidation catalysts oxidize a portion of the sulfur dioxide in the exhaust to sulfuric acid. The sulfur dioxide in the exhaust is formed by combustion of trace quantities of organic sulfur compounds in gasoline to sulfur dioxide. Gasoline contains an average sulfur level of 0.03% which is very low compared to other fuels. As a result, sulfur dioxide emissions from gasoline-fueled vehicles are less than 1% of the total sulfur dioxide emissions. Most sulfur dioxide emissions come from stationary sources.

The sulfur dioxide in the atmosphere is photochemically oxidized to sulfuric acid. Even if the oxidation catalyst converted all of the sulfur dioxide to sulfuric acid, the resultant sulfuric acid contribution from these vehicles would be less than 1% of the total sulfuric acid in the atmosphere.

However, it is possible to have high localized levels of sulfuric acid along heavily traveled roads. EPA has determined that the condition of most concern is a heavily traveled freeway with maximum traffic flow. EPA developed a driving cycle called the Congested Freeway Driving Schedule (the CFDS) with an average speed of 35 mph to represent this condition. During the past year, various companies have obtained extensive emission data using this cycle. Laboratory studies have also been done to determine how different parameters (e.g. catalyst composition) affect sulfuric acid formation. Work has also been done to measure sulfuric acid levels along roadways and to determine vehicle sulfuric acid emissions at higher mileages.

B. Mechanisms and Laboratory Studies

Experiments were conducted by GM, Ford, and Chrysler using laboratory apparatus or, in some cases, engine dynamometers or vehicles, to determine the effect of various parameters on sulfuric acid formation. The laboratory work performed was less extensive than that conducted in previous years when little was known about the formation of sulfuric acid over automotive catalysts.

GM studies showed that rhodium-containing catalysts produce less sulfuric acid than those containing only platinum or palladium. This confirms vehicle work done under an EPA contract with Exxon which showed that a rhodium-containing catalyst had unusually low sulfuric acid emissions.

Ford studies on the effect of noble metal composition on sulfuric acid formation show that it is possible to produce a palladium catalyst that forms less sulfuric acid than either a platinum-palladium catalyst or a platinum-rhodium catalyst. Additional Ford work shows that a rhodium-containing catalyst also has very low sulfuric acid emissions.

Ford conducted extensive engine dynamometer tests on 24 catalysts divided into four series (6 catalysts per series) to evaluate their sulfuric acid emissions. The catalysts were aged 100 hours for pre-conditioning prior to sulfuric acid testing. Catalyst light-off temperature and HC/CO conversion efficiency was measured at 800°F. Sulfuric acid measurements were made under conditions approximating 55 mph steady state operation of vehicle. Catalysts tested included Pt/Pd, Pt/Rh (with varying ratios of Pt/Rh), and platinum. The major finding of these tests is that rhodium-containing catalysts emit less sulfuric acid than catalysts without rhodium. There is a marked change with catalysts containing more than 10% rhodium, which emit far less sulfuric acid (about 10% conversion) than catalysts with less than 10% rhodium (about 40% conversion). Ford indicated that there is a loss in HC control with the increased rhodium content. However, it appears that the change in HC emissions is less than that for sulfuric acid.

Ford also conducted some laboratory studies on catalysts that have been installed on vehicles and operated for 50,000 miles. Formation of sulfuric acid was compared between the 50,000 mile Engelhard II B catalysts and fresh catalysts. It was found that the aged catalysts had much lower sulfuric acid formation depending upon factors such as presence of reducing gases (certain HC compounds and CO), and space

velocity. Even though the aged catalysts had high activity for propane and CO conversion, they had a two to six-fold decrease in sulfuric acid formation versus the fresh catalysts. These results are in accord with vehicle test data discussed later which show very low sulfuric acid emissions from catalyst vehicles with extended mileage.

GM conducted further experiments on the effect of temperature, space velocity, O_2 levels, and CO levels on sulfuric acid formation. It was found that low oxygen levels, higher CO levels, high catalyst temperature, and possibly low space velocity all lead to low sulfuric acid formation. These results are in complete agreement with previous tests run by GM, as well as past studies by Ford, Chrysler, other automobile manufacturers, and EPA contractors.

GM and Ford both reported results of laboratory studies on sulfuric acid storage. Storage of sulfuric acid occurs on fresh catalysts under most operating conditions, resulting in low sulfuric acid emission rates.

This effect is overcome on a vehicle, generally within the first 1000 miles. After that, high temperatures result in release of sulfuric acid (frequently as SO_2) with subsequent low temperature operation permitting storage once again. Since much of the stored sulfuric acid can be released as SO_2 at the higher temperatures, sulfuric acid emissions can be lower for systems which store significant quantities of sulfuric acid (e.g., pelleted catalyst systems). Again, this recent work agrees well with earlier work done by the automotive companies and EPA.

Ford reported some laboratory test results on both fresh and aged 3-way catalysts. The results on fresh catalysts show that all three 3-way catalysts tested (M-152C2-3, M-253, and M-257) have comparatively low sulfuric acid formation (e.g., 40% formation) compared with a fresh Engelhard II B oxidation catalyst under the same conditions (e.g., 80% formation of sulfuric acid). These data indicate that some 3-way catalyst formulations have inherently lower sulfuric acid formation than conventional oxidation catalysts independent of other conditions (i.e., O_2 level). Dynamometer-aged 3-way catalysts were also evaluated in the laboratory reactor apparatus. Three-way catalyst samples aged for 470 hours showed about 10% sulfuric acid formation in a laboratory reactor compared with about 50% sulfuric acid formation for fresh catalyst samples.

Chrysler did some limited studies using a vehicle (Car 685) to investigate the effect of CO and O_2 levels on sulfuric acid formation. Chrysler modified the exhaust system of this car to allow injection of known quantities of CO and O_2 . Sulfuric acid emissions were measured at 40 mph steady state conditions. The results of this work agree with earlier work showing that oxygen levels of 1% or less result in low sulfuric acid emissions (e.g., 1 mg/mi) while higher oxygen levels of 2% or more result in increased sulfuric acid emissions (e.g., 40 mg/mi or more).

Ford also did further work on how exhaust oxygen levels affect sulfuric acid emissions. A Pinto was equipped with a 3-way plus oxidation catalyst system. A managed air injection system (with a flow control valve in the secondary air flow upstream of the oxidation catalyst) was used to give variable amounts of oxygen (0.5%, 1%, 2%, and 5%). Complete test results are not available yet. Preliminary results suggest that lower oxygen levels result in lower sulfuric acid levels, but perhaps at the expense of some CO control.

Nissan has also done some engine dynamometer work on sulfuric acid using a 4-cylinder Datsun engine with either a pelleted or monolithic catalyst. This work shows a sharp increase in sulfuric acid emissions when the air-fuel ratio increases from 14.5 to 15.5 but only a moderate increase in sulfuric acid when the air-fuel ratio is increased further. This work also shows that monoliths and pellets emit the same quantity of sulfuric acid at temperatures over 600°C. Below this temperature, the monoliths tested by Nissan emitted more sulfuric acid presumably due to lower storage capacity. The Nissan work also shows lower sulfuric acid emissions from rhodium or barium (a stabilizer used in the substrate) containing catalysts. Additional work by Nissan shows sulfuric acid emissions to be greater for catalysts with more noble metal dispersed near the surface.

C. Sulfuric Acid Emission Data

GM tested seven of the 1975-76 vehicles used in their Sulfuric Acid Dispersion Experiment. These vehicles were tested on a driving schedule similar to the driving experienced around the GM Proving Ground track during the Sulfuric Acid Dispersion Experiment. This test cycle took two hours to complete with sulfuric acid measurements being taken every half hour (i.e., four measurements over two hours). The fuels used contained 0.032 wt. % sulfur. The vehicles were tested at both the GM Proving Ground and Research Labs. The last sulfuric acid measurement for each vehicle is listed in Table 1.

These tests showed an overall sulfuric acid emission rate of 51 mg/mi emission rate calculated for the entire 352 car fleet used for the Sulfuric Acid Dispersion Experiment. There is reasonably good agreement between the two laboratories.

GM also measured sulfuric acid emissions from 12 other 1975-76 production vehicles, using the Congested Freeway Driving Schedule (CFDS). It is assumed that 0.032 wt. % sulfur fuel was used. These results are shown in Table 2.

TABLE 1

Sulfuric Acid Emissions from
Dispersion Experiment Cars

<u>Car</u>	<u>Lab*</u>	<u>Sulfuric Acid (mg/ml)</u>
'75 302 Ford (Federal)	GM PG	31.8
	GM RL	41.1
'76 302 Ford (Federal)	GM PG	73.8
	GM RL	61.0
'75 Chevrolet (Federal)	GM PG	14.4
	GM RL	14.0
'75 Chevrolet (California)	GM PG	69.6
	GM RL	94.0
'75 Chevrolet (California)	GM PG	73.9
	GM RL	98.8
'75 318 Chrysler (California)	GM PG	84.6
	GM RL	78.2
'76 Pontiac	GM PG	32.7
	GM RL	55.1

*Proving Ground = PG
Research Labs = RL

TABLE 2
Sulfuric Acid Emissions from
GM Production Cars

<u>Car</u>	<u>Emission Control System</u>	<u>Sulfuric Acid (mg/ml)</u>
'75 Cadillac	California AIR	79
'75 Oldsmobile	California no AIR	17
'75 Nova	California AIR	136
'75 Vega	California AIR	18
'75 Vega	Federal pulsed AIR	1
'76 302 Ford	Federal AIR	58
'76 Cutlass	California no AIR*	17
'76 Cutlass	Federal no AIR	2
'76 Cutlass	California no AIR	2
'76 Cutlass	California AIR	44
'76 Nova	Federal no AIR	0.3
'76 Nova	Federal no AIR	0.3

*3.6% exhaust O₂ for this car; O₂ not measured for other cars

These test results show that cars with air injection and presumably high exhaust oxygen levels have high sulfuric acid emissions while cars without air pumps and presumably low exhaust oxygen levels have much lower sulfuric acid emissions. Unfortunately, GM did not measure oxygen levels from these cars which would be useful in interpreting these results. Also, GM did not report the mileage of these vehicles.

Ford has measured sulfuric acid emissions from two 1976 Ford LTDs, a California version and a Federal version, both with the 400 CID engine. Ford not only obtained emission data on these cars but also investigated the effects of spark timing, EGR, oxygen concentration, and catalyst composition on sulfuric acid formation.

With the Federal car, Ford found high sulfuric acid emissions (about 50-60 mg/mi) with oxygen levels from 1% to 5%. Under 1% oxygen, the sulfuric acid emission levels decreased dramatically to under 20 mg/mi (as low as about 5 mg/mi in one test with about 0.3% oxygen). However, sulfuric acid emissions were under 10 mg/mi on this car over the CFDS with oxygen levels anywhere from 1.5% to 6.5%. It is unusual to see significantly higher sulfuric acid emissions at a steady state speed than over the CFDS. Other work conducted by EPA, GM, Exxon, Southwest Research Institute, and Chrysler did not indicate this phenomenon. Perhaps the higher sulfuric acid emissions are due to lower "spikes" of reducing gases such as HC and CO over a steady state mode versus a transient driving cycle. It could be that the particular Ford tested was more sensitive to such a phenomenon than other vehicles. It could also be that the immediate preconditioning before the CFDS resulted in purging of stored sulfuric acid with subsequent storage over the CFDS. It was found that changing the spark timing (from 6° to 16° BTDC) and plugging the EGR did not affect sulfuric acid over the CFDS.

Ford investigated the effect of using Pb/Pd, Pt/Rh, or Pd catalysts all with the same substrate on both the California and Federal cars. Results of the tests on these catalysts are shown in Table 3. These results show that Pt/Rh catalysts do not always give lower sulfuric acid emissions than other catalysts.

Ford Also ran tests comparing different versions of the CFDS denoted as SET 7 and SET 7D. The SET 7 is extremely difficult if not impossible for the driver to follow all the time while the SET 7D has the "noise" modified by removing those parts difficult for the driver to follow. Furthermore, the present requirements outlining allowable driver tolerances for the FTP (± 2 mph within 1 sec) resulted in the earlier

TABLE 3

Sulfuric Acid Emissions of Different Catalysts

<u>Vehicle</u>	<u>Catalyst</u>	<u>Driving Cycle</u>	<u>Sulfuric Acid (mg/mi)</u>
Ford - Federal	Pt/Pd	45 mph	70
	Pt/Rh	45 mph	28
	Pd	45 mph	10
	Pt/Pd	CFDS	10
	Pt/Rh	CFDS	10
	Pd	CFDS	8
Ford - California	Pt/Pd	CFDS	28-40
	Pt/Rh	CFDS	25
	Pd	CFDS	42

SET (the one with high "noise") having different drivers following the CFDS in different ways. That is, a driver could either follow or not follow the "noise" and still have a valid CFDS. Since the "noise" was difficult to follow, many drivers would not follow it. The modified CFDS (SET 7D) is easy enough for the average driver to follow the "noise" so that most cycles would be driven the same. Ford ran a total of about 6 SET 7 and 7Ds on a 1976 California Ford. Both cycles gave about 50 mg/mi sulfuric acid emissions with the SET 7D being about 18% lower than the SET 7. These results are in general agreement with those obtained by EPA even though the Ford results show greater differences. Extensive EPA tests (both in-house and at Southwest Research) on about 20 repetitions of the CFDS (both without any noise whatsoever, a precursor of SET 7, and SET 7D) show the SET 7D to have about 15% lower sulfuric acid emissions.

Chrysler ran sulfuric acid tests on two 1976 production vehicles. The first car (Car 176, a Dodge Coronet equipped with a 318 CID engine, a 90 cu. in. catalyst, and an air pump) showed very high sulfuric acid emission (82 mg/mi) over the CFDS. The second vehicle (Car 155, a Dodge Dart equipped with a 225 CID engine, a 90 cu. in. catalyst, and an air pump) showed much lower sulfuric acid emissions (9.4 mg/mi) over the CFDS.

Most of the test results on prototype cars are somewhat higher than those found in the EPA baseline study. This study involved sulfuric acid testing of 78 current and future prototype cars. These tests showed catalyst cars without air injection to emit about 10 mg/mi sulfuric acid while catalyst cars with air injection emitted about 20 mg/mi sulfuric acid.

D. Decrease in Sulfuric Acid Emissions with Extended Mileage

Very extensive sulfuric acid emission data have been taken on oxidation catalyst vehicles at low mileages. The bulk of these data were taken in 1975 and summarized in the EPA Status Report on Sulfate Emission Control Technology as well as the EPA Report on Sulfate Emission Control Technology and the EPA Report on the Baseline Study. In the Baseline Study, about 60 vehicles were tested for sulfuric acid emissions. However, almost no sulfuric acid data have been taken on vehicles at extended mileage. EPA funded a major contract with Southwest Research Institute to measure sulfuric acid emissions on four catalyst vehicles as they accumulated 50,000 miles. Exxon Research and Engineering funded an in-house study to accumulate 50,000 miles on 20 cars and measure sulfuric acid emissions at various intervals. Both studies showed a significant decrease in sulfuric acid emissions occurring at roughly 20,000 miles. While sulfuric acid emissions can be high initially, most of the vehicles had emissions below 10 mg/mi after the drop occurred.

As a result of this work, EPA has asked the following companies to measure sulfuric acid emissions about every 5,000 miles on certain vehicles as they accumulate AMA type mileage.

<u>Manufacturer</u>	<u>Number of Vehicles to be Tested</u>
GM	12 cars
Ford	8
Chrysler	6
AMC	2
Toyota	2
Datsun	2
VW	2

These cars would probably come from existing fleets accumulating mileage (e.g., precertification fleet) to keep the cost of such a program at a lower level. The manufacturers have indicated their willingness to participate in this program and to have these tests completed by the end of 1977.

Aside from this program, both GM and Ford have reported current data on sulfuric acid emissions of cars at higher mileages.

GM is testing six vehicles (1975 Impalas) in a GM transportation pool as they accumulate mileage. Four of these cars were designed to meet the 1976 California standards while the other two cars are Federal cars. The cars currently have from 5,000 to 15,000 miles. The results to date are given in Table 4 for the CFDS and 60 MPH cruise. These results show a marked degradation in sulfuric acid emissions over the CFDS but very little degradation during 60 mph test conditions. Additional emission testing will be done as these cars accumulate mileage. GM did not report gaseous emissions (HC, CO, NO_x) from these cars.

Ford ran a series of sulfuric acid emission tests on some of their 50,000 mile 1977 certification cars. The following test sequence was used with 0.03% sulfur fuel:

TABLE 4

GM Sulfuric Acid Tests of
Transportation Pool Cars

<u>Car</u>	<u>Mileage</u>	<u>Fuel Sulfur</u>	<u>Sulfuric Acid Emissions (mg/mi)</u>	
			<u>CFDS</u>	<u>60 mph</u>
R5947 (Federal)	700	0.004%	0.3	7
	5000		0.4	9
R5949 (California)	600	0.004%	6	16
	10000		1	14
	15000		0.8	12
R5951 (California)	1800	0.004%	2	14
	5000		0.8	15
R5948 (Federal)	1700	0.036%	4	45
	5000		3	73
	11000		2	76
	15000		1	58
R5950 (California)	600	0.036%	108	134
	5000		55	111
	10000		15	132
R5952	800	0.036%	64	112
	10000		36	121
	15000		14	106

222 miles AMA preconditioning
LA-4 prep followed by cold soak
FTP
505 sec of LA-4
2 minutes idle
CFDS
10 minutes idle
CFDS
10 minutes idle
CFDS
10 minutes idle
CFDS
10 minutes idle
HFET

Each test was repeated on two additional days. Ford also tested three 1976 California Capri vehicles at 4,000 miles. The test results are given in Table 5. All of the vehicles had Pt/Pd catalysts and are 50,000 mile vehicles unless noted otherwise.

These vehicles frequently, but not always, show low sulfuric acid emissions at 50,000 miles. However, three of the cars had significantly higher sulfuric acid emissions (18-108 mg/mi) than the others. Ford points out that two of these cars also had low CO emissions, showing an inverse relationship between CO and sulfuric acid for this system. Ford is also measuring sulfuric acid on some of the 1978 certification cars.

E. Sulfuric Acid Emissions from Future Prototypes

GM tested 12 future prototype vehicles for sulfuric acid emissions. These vehicles included lean burn and 3-way catalyst vehicles. The lean burn vehicles had higher sulfuric acid emissions while the 3-way catalyst vehicles had low sulfuric acid emissions. The results of these tests for the CFDS are given in Table 6. GM did not supply gaseous emission results or any other details on the control systems other than what is listed in the table.

Ford measured sulfuric acid emissions from a variety of oxidation catalyst, 3-way and oxidation catalyst, and dual catalyst cars designed to meet low NO_x standards. Even though two of the oxidation catalysts had 50,000 miles on them, the sulfuric acid emissions were still significantly high. The sulfuric acid emissions from the 3-way catalyst/oxidation catalyst prototypes were also high, because of SO₂ oxidation occurring over the oxidation catalyst with air injection before the oxidation catalyst. The conventional 3-way catalyst would, of course, be expected to have very low sulfuric acid emissions. Finally, Ford found high sulfuric acid emissions (69 mg/mi) from the Gould dual catalyst system. Independent EPA tests confirm that the Gould dual catalyst system does have high sulfuric acid emissions. The results of the Ford tests are given in Table 7 for the CFDS.

TABLE 5

**Ford Sulfuric Acid Test Results
on 1976-77 Cars**

<u>Vehicle</u>	<u>Engine Disp.</u>	<u>Catalyst</u>	<u>Sulfuric Acid Emissions - CFDS (mgpm)</u>	<u>FTP Emissions (gm/ml)</u>		
				<u>HC</u>	<u>CO</u>	<u>NOx</u>
4A	2.3 litre	EI	0.51	0.20	2.86	1.29
5A	2.3 litre	MB	0.61	0.15	5.20	1.03
11A	2.3 litre	UOP	6.07	0.10	2.62	1.65
10A	2.3 litre	MB	0.61	0.11	4.47	1.75
10A	2.3 litre	MB	0.72	0.05	1.53	1.54
10A	2.3 litre	MB	0.47	0.05	1.72	1.50
21B	2.3 litre	EI	0.64	0.10	2.92	1.31
8A	2.8 litre	EI	1.67	0.12	2.16	0.96
14A	250 CID	UOP	1.98	0.16	5.25	0.93
16A	302 CID	UOP	45.65	0.10	0.66	1.13
17B	302 CID	UOP	107.80	0.07	0.12	0.94
14B	400 CID	EI	1.34	0.23	9.57	1.06
14B	400 CID	EI	1.79	0.15	7.88	1.02
21A	400 CID	EI	17.60	0.15	3.13	2.33
5C13*	2.3 litre	MB	21.57	0.08	0.12	1.00
5C15*	2.3 litre	MB	31.62	0.07	0.76	1.10
5C16*	2.3 litre	MB	9.39	0.07	0.44	0.64

*1976 California 4K Vehicle

TABLE 6
Sulfuric Acid Tests on Prototype Vehicles

Car	Control System	Fuel Sulfur Level	Exhaust Oxygen Level	Sulfuric Acid (mg/ml)
74 Chevelle	lean burn engine, production catalyst	0.06%	2.1%	99
74 Chevelle	lean burn engine, production catalyst	0.031%	2.1%	42
74 Chevrolet	closed loop fuel injection, 3-way catalyst	0.06%	0.7%	0.2
74 Chevrolet	closed loop fuel injection, 3-way catalyst	0.06%	0.3%	0.1
74 Chevrolet	closed loop carburetor, 3-way catalyst	0.031%	0.7%	0.2
74 Oldsmobile	production catalyst, no AIR	0.031%	1.5%	44
74 Oldsmobile	production catalyst, no AIR	0.031%	1.6%	76
75 Chevelle	production catalyst, AIR	0.031%	1.5%	41
74 Chevelle	production catalyst, warm-up catalyst, AIR	0.031%	1.5%	15
75 non-GM	stratified charge engine, fuel injection, monolith catalyst	0.012%	0.5%	6
76 Chevelle	production catalyst, AIR switching	0.031%	1.5%	4

TABLE 7

Ford Sulfuric Acid Tests
on Low NOx Prototypes

<u>Vehicle</u>	<u>HC</u> <u>gm/mi</u>	<u>CO</u> <u>gm/mi</u>	<u>NOx</u> <u>gm/mi</u>	<u>H₂SO₄</u> <u>mg/mi</u>
8D1-302-5P (50K oxidation catalyst)	0.06	0.01	0.57	139.4
	-	-	-	103.2
	0.06	0.03	0.58	107.1
	0.07	0.00	0.61	110.9
	0.07	0.05	0.64	162.1
	-	-	-	106.9
	0.01	0.00	0.62	114.5
	0.05	0.01	0.62	115.4
	0.06	0.02	0.57	88.5
	-	-	-	86.8
	0.06	0.05	0.56	95.0
	0.06	0.03	0.56	87.8
	0.05	0.02	0.65	103.6
	-	-	-	95.6
	0.05	0.04	0.62	92.3
	0.05	0.00	0.62	104.6
8D1-302-5P (oxidation catalyst from 8D1-302-6P, 50K)	0.03	0.02	0.65	102.5
	0.03	0.02	0.60	117.9
	-	-	-	119.7
	0.04	0.01	0.65	106.8
8D1-302-6P (50K oxidation catalyst)	0.09	0.68	0.46	12.6
	-	-	-	19.9
	0.07	0.66	0.47	17.4
	0.09	1.06	0.42	13.7
	-	-	-	12.8
	0.08	0.97	0.42	14.4
	0.08	0.83	0.43	15.3
	0.15	0.16	0.60	56.2
8D1-302-1P (3-way and oxidation catalysts)	-	-	-	51.2
	0.16	0.14	0.70	61.4
	0.15	0.13	0.67	62.3
	0.16	0.17	0.55	69.8
	-	-	-	53.6
	0.18	0.14	0.55	71.4
	0.18	0.18	0.56	61.2

(TABLE 7 cont'd)

8D1-302-7P (3-way and oxidation catalyst)	0.14	0.40	0.49	27.9
	-	-	-	33.3
	0.13	0.43	0.50	25.8
	0.14	0.29	0.49	34.5
	0.13	0.28	0.61	37.4
	-	-	-	43.0
	0.13	0.20	0.67	45.7
	0.14	0.26	0.64	40.1
Gould catalyst (1975 400 CID LTD)	0.33*	0.46*	0.25*	
	0.28	0.39	0.17	69.0

*FTP data

Chrysler has run sulfuric acid emission tests on advanced prototype vehicles including the lean burn (with and without oxidation catalyst), start catalyst, and dual catalyst (Gould reduction catalyst followed by an oxidation catalyst) vehicles. The lean burn vehicles (cars 209 and 271) without catalyst showed very low sulfuric acid emissions while the lean burn vehicle (Car 4028) with oxidation catalyst showed higher sulfuric acid emission (41 mg/mi). Chrysler tested three start catalyst systems (Cars 454, 332, and 270) which were 1977 California prototypes. All three cars had 22 cu. in. start catalysts and 90 cu. in. main oxidation catalysts with air pumps. These three cars produced 53, 25, and 62 mg/mi sulfuric acid emissions over the CFDS which is in the same range as that expected from conventional oxidation catalysts without start catalysts.

Chrysler tested three dual catalyst type vehicles. The first of these, Car 178, had a Gould reduction catalyst followed by a 152 cu. in. monolithic catalyst with an air pump. This car emitted a very low 5.4 mg/mi sulfuric acid over the CFDS which is similar to values Chrysler reported in 1975. The second car, Vehicle 232, has a monolithic Chrysler reduction catalyst followed by a 90 cu. in. oxidation catalyst and air pump. This vehicle also produced very little sulfuric acid (13-25 mg/mi over the CFDS). The third vehicle (Car 623) also has a monolithic Chrysler reduction catalyst followed by a 90 cu. in. oxidation catalyst. This car has an air modulation system which injects about 7% oxygen upstream of the reduction catalyst for the first 90 seconds after a cold start. After this, sufficient air is injected into the oxidation catalyst to result in a 2% oxygen level (a diverter valve is used to achieve this). With the 2-3% oxygen level, 11.1 mg/mi of sulfuric acid is emitted over the CFDS. However, if the diverter valve is inoperative and all of the air is injected into the oxidation catalyst (7% oxygen), sulfuric acid emission levels of 46.3 mg/mi are observed over the CFDS.

The sulfuric acid emission results for the start catalyst and dual catalyst systems over the CFDS are given in Table 8.

F. Sulfuric Acid Traps

GM is the only company reporting information on sulfuric acid traps. EPA has also done extensive work on sulfuric acid traps through a contract at Exxon Research and Engineering. The sulfuric acid trap is simply a chemical placed in a container (a muffler or catalyst-like container is satisfactory) on the vehicle after the oxidation catalyst. All of the exhaust passes through this container allowing the sulfuric acid to react with the sorbent.

The EPA work at Exxon showed several promising sorbents, the most promising of which was 85% CaO, 10% Al₂O₃, and 5% Na₂O. This sorbent can be fashioned into either pellets or rings. Tests on the sorbent show extremely high efficiency (about 90%) in trapping sulfuric

TABLE 8

Chrysler Sulfuric Acid Test Results

<u>Vehicle</u>	<u>Sulfuric Acid (mg/ml)</u>	<u>Oxygen %</u>	<u>CO %</u>
454 (start catalyst)	51.4	6.4	0.099
	59.4	4.9	0.466
	49.7	4.8	0.649
	13.6	3.2	0.850
	17.1	3.2	0.822
332 (start catalyst) Right Exhaust	14.5	3.0	0.220
	18.5	4.0	0.270
	12.9	4.0	0.304
	14.2	4.0	0.308
Left Exhaust	7.6	3.0	0.060
	14.8	4.0	0.043
	10.0	3.7	0.078
	13.2	4.0	0.068
Left Exhaust Dummy Main	2.9	4.0	0.090
Left Exhaust Dummy Start	6.8	3.3	0.358
	16.9	3.7	0.268
270 (start catalyst)	61.8	4.8	0.134
178 (dual catalyst)	5.4	2.2	3.257
232 (dual catalyst)	13.1	5.3	2.949
	15.6	6.1	2.267
	25.1	6.1	1.732
623 (dual catalyst)	11.1	3.3	2.66
	46.3	7.3	1.29

acid even after extended mileage (25,000 miles). However, the sorbent swells causing an unacceptably high pressure drop causing the vehicle to lose power and increase its fuel consumption. EPA and Exxon spent a second year in a contract extension to try to remedy these problems and were unsuccessful. The second year Exxon program did identify a number of sorbents that could be considered promising. The overall conclusion of the EPA-Exxon work is that, if vehicle sulfuric acid reductions are needed, the sulfuric acid trap is a potentially promising candidate but will need a very large development effort. Even with a large development effort, it is not certain that a viable sulfuric acid trap would result.

In their work, GM screened many different sulfuric acid sorbents and found two promising candidates, CaO and a $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ sorbent. The latter sorbent is especially attractive in that it is sufficiently selective that sulfuric acid alone with no SO_2 is trapped. A vehicle test on the CaO material showed 95% efficiency when fresh but only 70% efficiency (over the CFDS) or 40% efficiency (at 40 mph) after 32,000 km.

The $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ trap has been tested only 1600 km and shows no loss in efficiency. Even though the GM program is less extensive than the EPA-Exxon program, the GM results seem to be in agreement with those of EPA-Exxon.

G. Sulfate Measurement Methods

Both GM and Ford reported work on measurement methods for sulfuric acid. This work involves both the collection methods used for automotive sampling and the analytical methods used on the collected samples.

GM has investigated CVS flow rate and concludes that either a 300 or 600 CFM flow rate is adequate for a large (18-inch diameter - 20-foot length) dilution tunnel. However, GM feels that a lower flow rate of 335 CFM will not work with a smaller dilution tunnel (8.4-inch diameter - 10-foot length) due to high sulfuric acid losses. The 335 CFM flow rate is used on almost all current CVS units. GM also stated that sample zone temperatures of over 200°F will result in lower sulfuric acid values (possibly by loss of sulfuric acid from the filter or incomplete condensation of sulfuric acid). GM also found that tunnel inlet temperatures of less than 200°F (caused by long connecting tubing between the vehicle and tunnel) cause low sulfuric acid readings. GM stated that smaller variations in paired samples were noted with critical flow venturi sampling versus CVS sampling. All of these items are being investigated by an EPA contract currently in progress at Southwest Research.

GM also stated that neither 5300 nor 25,000 CFM cooling fans result in vehicle temperatures during dynamometer operation that are typical of on-road operation. EPA generally uses a combination of several 5300 CFM fans to assure adequate cooling; EPA has also purchased a 25,000 CFM fan. EPA has just started a contract with Olson Laboratories to investigate the configuration of cooling fans that will result in vehicle cooling approximating that occurring during road operation.

Finally, GM notes that their work shows the perchlorate titration system to be equivalent to the barium chloranilate system for analysis of filter samples containing sulfuric acid. Ford has done similar work. EPA work also shows both systems are equivalent.

Ford has extensive work (both in-house and some EPA contract work) in progress investigating analytical methods for sulfuric acid and SO_2 . Ford is currently working on an instrument for continuous SO_2 measurement of automotive exhaust. Furthermore, Ford is doing some work on analysis of sulfuric acid by mass spectrometry. In particular, electron impact mass spectral analysis offers the potential of distinguishing between sulfuric acid itself and salts of sulfuric acid (ammonium sulfate). Such instrumentation would be very useful in ambient air monitoring, where sulfuric acid particles could be distinguished from its salts. Such distinction is valuable since the two compounds probably have different health effects.

H. Correlation of Sulfuric Acid Tests Among Different Laboratories

During the past year, several vehicles tested by GM and Ford have also been tested by EPA. Vehicles tested by the GM Proving Ground were also tested by EPA in the Sulfuric Acid Baseline Program. These tests showed generally good agreement between the laboratories.

Ford recently completed construction of dilution tunnels at their Scientific Research Laboratory and another Dearborn Laboratory. Ford tested a 1976 vehicle equipped with a 400 CID engine at both of their facilities and sent the car to EPA for correlation testing. The test results show reasonably good (but not complete) agreement among the three laboratories in the sulfuric acid emission values obtained.

As part of the sulfuric acid deterioration factor program to be conducted by the manufacturers and EPA during the coming year, sulfuric acid correlation testing will be needed among the different laboratories. A round robin car will be used for this purpose.

I. Roadside Sulfuric Acid Levels

Both the GM and Ford submissions discussed work on measuring roadside levels of sulfuric acid. In particular, GM completed a major experiment this past year titled the Sulfate Dispersion Experiment. This work involved running 352 cars, equipped with catalysts and air pumps (designed for the 1976 California standards), around a loop at the GM Proving Grounds. The cars were preconditioned with 0.032% sulfur fuel and operated at about 55 mph. The average sulfuric acid vehicle emission rate during these tests was about 0.037 mg/mi. Ambient air levels of sulfuric acid were monitored. Also, a tracer gas (SF_6) was emitted from eight pickup trucks participating in the experiment. Measuring the level of SF_6 and sulfuric acid under various meteorological conditions allowed verification of an EPA predictive air quality model and also gave an independent measurement of roadside sulfuric acid levels.

It was found the normal levels of sulfuric acid in the air samples due to the vehicles were 3-5 $\mu\text{g}/\text{m}^3$. Under adverse meteorology, increments of 15 $\mu\text{g}/\text{m}^3$ were found. The increased level of sulfuric acid inside the vehicles was also measured and found to be about 4 $\mu\text{g}/\text{m}^3$. There was very good agreement between results obtained with the SF_6 tracer and the sulfuric acid measurements.

These results showed that the EPA Highway Model overpredicts sulfuric acid emissions at the pedestrian level downwind from the roadway. The overprediction occurs for stable meteorological conditions and gets worse as the wind speed decreases (when roadside sulfuric acid levels would be highest). The EPA Highway Model is more or less satisfactory under unstable meteorological conditions (when sulfuric acid levels along roadsides would be much lower). Apparently, "mechanical mixing" due to traffic flow is an important parameter and not accounted for in the EPA Highway Model. Various government agencies (EPA, DOT, and DHEW) as well as other automobile companies helped participate in this work.

In addition to the massive GM experiment, Ford has been conducting monitoring experiments in the Allegheny Tunnel on the Pennsylvania Turnpike. Initially, Ford monitored rubber tire particulate there and then diesel and sulfuric acid particulate. The cars driving through the tunnel would be those designed for the Federal standards and therefore have lower sulfuric acid emission rates than the California cars used in the GM experiment. However, to date, no sulfuric acid increment has been noted from the introduction of catalyst cars.

J. Conclusions

Work during the past year confirmed earlier studies showing that exhaust oxygen levels are the most important single parameter affecting sulfuric acid emissions. Low exhaust oxygen levels (such as

those found with 3-way catalyst cars) can result in sulfuric acid emission levels from catalyst cars of under 5 mg/mi which is equivalent to levels found with non-catalyst cars.

Sulfuric acid tests on current catalyst cars run this past year agree well with previous tests. Oxidation catalyst cars without air injection usually emit under 10 mg/mi of sulfuric acid. Current oxidation catalyst cars with air injection emit greater quantities of sulfuric acid, generally 20 mg/mi or higher. Tests of advanced oxidation catalyst vehicle prototypes (which generally have air injection) show similar sulfuric acid emission levels. Prototype 3-way catalyst cars with a down-stream oxidation catalyst and air injection show sulfuric acid emission levels similar to conventional oxidation catalyst cars equipped with air injection.

One major area needing additional investigation is the effect of mileage on sulfuric acid emissions. Limited test results so far show high mileage oxidation catalyst vehicles have lower sulfuric acid emissions. Sulfuric acid emissions are reduced by a factor of two and, in some cases, even more. Some results have even approached the level of non-catalyst cars (1 mg/mi). Significant data are still needed to determine whether this reduction with extended mileage is such that sulfuric acid emissions are not a problem. The car companies are running tests on catalyst vehicles as they accumulate mileage to determine the extent of this reduction.

Finally, during the past year, GM completed a major test track experiment measuring roadside sulfuric acid levels. This work showed roadside sulfuric acid levels far below levels predicted by EPA air quality models. These lower levels, combined with a possible reduction in sulfuric acid emissions at higher mileages, may result in sulfuric acid emissions being considered much less of an air quality problem than was previously the case.

III. HYDROGEN CYANIDE

A. Introduction and EPA Work

In 1974, it was reported by Bell Laboratories that automotive catalysts could, under very unusual conditions in a laboratory reactor, form hydrogen cyanide (HCN) from laboratory gases. EPA found in early 1976 that vehicles using a 3-way catalyst could produce HCN under rich malfunction modes. Since Volvo and Saab were certifying 3-way catalyst systems for use in California in 1977, EPA had to make a rapid determination on the levels of HCN that would be acceptable from a health standpoint. EPA was concerned primarily about the worst case situation, i.e.,

localized levels of HCN that could occur in indoor parking garages and along heavily traveled roadways. The highest HCN emissions were observed under rich malfunction modes when CO emissions were also highest (approaching levels found in some uncontrolled pre-1968 vehicles).

EPA considered two types of worst case situations in determining acceptable levels for HCN exposure in localized areas. The first was a closed environment situation (i.e., garage-type exposure) while the second was a highway-type exposure situation. In the closed environment situation, an upper bound of 5 ppm HCN could result from a maximum raw exhaust level of 10 ppm. The corresponding CO level under these conditions would be 6500 ppm. The adverse health effects of CO would overshadow possible adverse effects of HCN by more than two orders of magnitude. For the highway type exposure, a 150 mg/mi HCN emission rate would result in a 1.1 ppm HCN level with 17,000 vehicles/hour along a heavily traveled freeway, under the worst meteorological situation, with each car emitting the maximum amount of HCN. EPA-ORD states that 1 ppm HCN exposure would not have unacceptable health effects.

It was also thought that a primary factor affecting HCN formation was the rhodium content of the catalyst. The Engelhard catalysts planned for use by Volvo contained about 16% rhodium. Most 3-way catalysts contain rhodium, sometimes at lower levels (e.g., 7%). Many oxidation catalysts also contain small amounts of rhodium (i.e., 7% or less). Some 1975 Ford oxidation catalysts (those made by Matthey Bishop) and oxidation catalysts used by many of the foreign manufacturers contain rhodium.

EPA therefore required that all 1977 certification cars equipped with rhodium catalysts be tested by EPA-ORD for HCN emissions. All such cars tested to date have been below the HCN levels that had been established as safe with a large margin of safety on a preliminary basis by EPA.

Typical data found for a Volvo equipped with a 3-way catalyst by EPA-ORD are given in Table 9.

Another Volvo 3-way catalyst system (Car 7712) was tested by Exxon Research and Engineering under both normal and malfunction conditions. The rich malfunction mode was induced by disconnecting the oxygen sensor. Instead of the pyridine-pyrazolone wet chemistry method used by EPA for HCN analysis, Exxon used a selective ion electrode method. The results of the Exxon tests are shown in Table 10.

TABLE 9

EPA-ORD Test Results on Volvo
(Rich Malfunction)

<u>Test</u>	<u>HC</u> <u>gm/mi</u>	<u>CO</u> <u>gm/mi</u>	<u>NOx</u> <u>gm/mi</u>	<u>HCN</u> <u>mg/mi</u>	<u>NH₃</u> <u>mg/mi</u>	<u>H₂S</u> <u>mg/mi</u>	<u>COS</u> <u>mg/mi</u>
Idle*	0.32	4.42	0.062	1.70	7.9	0.47	0.03
FTP	1.66	40.5	0.503	66.3	493	6.88	1.89
CFDS	1.13	28.2	0.314	110.6	627	10.1	2.11
HFET	0.88	22.4	0.383	78.8	735	7.59	1.72
30 mph	0.84	24.5	0.032	16.4	110	NA	1.32
40 mph	0.80	20.3	0.07	47.1	176	NA	0.71
50 mph	0.94	23.9	0.21	113.8	270	NA	1.16

*g/minute

TABLE 10

Exxon Tests Results on Volvo

<u>Test</u>	<u>HC</u> <u>gm/mi</u>	<u>CO</u> <u>gm/mi</u>	<u>NOx</u> <u>gm/mi</u>	<u>HCN</u> <u>mg/mi</u>	<u>NH₃</u> <u>mg/mi</u>
<u>NORMAL OPERATING CONDITIONS:</u>					
Idle*	0	0	0.45	0.4	5.8
FTP	0.21	2.70	0.32	2.3	36.5
CFDS	0.08	0.55	0.11	1.9	29.1
FET	0.05	0.31	0.08	2.6	28.3
30 mph	0.06	0.88	0.02	1.0	10.6
40 mph	0.03	0.08	0.16	0.6	10.6
50 mph	0.06	0.45	0.08	0.6	43.8
<u>RICH MALFUNCTION MODE:</u>					
Idle*	2.97	29.12	0.43	0.4	9.4
FTP	1.08	24.97	0.74	22.5	327.8
CFDS	0.77	17.19	0.63	21.7	493.9
FET	0.68	14.36	1.14	19.3	425.4
30 mph	0.76	19.27	0.14	29.0	187.1
40 mph	0.90	15.97	0.50	62.0	481.4
50 mph	0.85	24.55	0.68	146.5	749.0

*g/minute

It can be seen from these data that HCN emissions are negligible under normal operating conditions. However, HCN emissions definitely increase under rich malfunction conditions to levels as high as 110 mg/mi.

Rhodium-containing oxidation catalyst also has the potential of producing HCN under rich malfunction conditions. Since oxidation catalysts generally contain less rhodium than some 3-way catalysts, they would be expected to produce far less HCN. EPA-ORD tests on three VW 1977 certification cars show this to be true. The test results for one of these cars (an Audi 100) are given in Table 11.

Test results for two other VW certification cars (an Audi 80, Car 8389 and a VW Rabbit, Car 6846) were similar. The highest HCN emissions observed for these three cars was 7 mg/mi for the VW Rabbit over the FTP under the rich malfunction mode.

B. GM Work

In the 1975 Status Report, GM discussed tests they ran on non-catalyst cars and 1975 vehicles for HCN emissions. The non-catalyst cars emitted 11-14 mg/mi which should be considered the baseline with which all of the catalyst cars should be compared. The 1975 oxidation catalyst production cars emitted about 2 mg/mi.

In the 1975-76 work discussed in the most recent report, GM tested several additional cars for HCN emissions using a modified colorimetric method. The first cars tested were two 1975 GM production cars (Cars R5454 and R5452) designed to meet California standards with the standard Pt-Pd pelleted catalyst. The first car was tested with the air pump disconnected to enrich the exhaust. CO emissions were lower (5.1 gm/mi) with the air pump disconnected than when it was connected (8.9 gm/mi). Under either condition, HCN emissions were very low at 2 mg/mi. The second car was run with both the standard and a specially designed rich operating carburetor. HCN emissions were very low under both conditions being 2 and 0 mg/mi respectively, while CO was 3.1 and 96.1 gm/mi. While GM does not specify test conditions, it is assumed these cars were tested on the FTP.

GM also tested two experimental cars for HCN emissions (Cars CH42216 and ES66344). The first vehicle contained an experimental 3-way catalyst (HN-2217) and a closed-loop carburetor with an oxygen sensor. This car had FTP emissions of 3.1 HC, 85.5 CO, 0.7 NO. However, HCN emissions were only 4 mg/mi. Presumably, this vehicle was operating under a malfunction condition giving the high CO emissions.

TABLE 11
EPA-ORD Test Results on VW Certification Cars

<u>Vehicle</u>	<u>Test</u>	<u>HC</u> <u>gm/mi</u>	<u>CO</u> <u>gm/mi</u>	<u>NOx</u> <u>gm/mi</u>	<u>HCN</u> <u>mg/mi</u>
Audi 100 (Car 5202, certifica- tion tune)	FTP	0.18	1.94	1.24	3.03
	CFDS	0.13	0.72	1.40	1.40
	FET	0.11	0.62	1.40	0.97
	Idle	0.01	0.12	0.02	0
	(925 rpm)*				
	Idle	0.12	0.03	0.05	0
	(2000 rpm)*				
Audi 100 (Car 5202, rich mal- function, 1.6% CO)	FTP	0.36	9.92	1.15	5.65
	CFDS	0.22	3.83	1.05	3.37
	FET	0.12	1.44	1.16	1.09
	Idle	0.11	4.28	0.02	1.08
	(925 rpm)*				
	Idle	0.02	0.11	0.05	0.08
	(2000 rpm)*				

*g/minute

The second car was a Vega with electronic fuel injection, an oxygen sensor, and Degussa experimental 3-way catalyst (HN-3032). This vehicle was tested under both normal operating conditions and rich malfunction conditions. The rich malfunction was induced by enriching the car electronically in the open loop mode. The highest HCN value found in these tests was 18 mg/mi which is only slightly higher than HCN values found with non-catalyst cars during previous tests. The car was then retested in the closed-loop mode using an HN-3032 catalyst that had been aged 50,000 miles. HCN emissions were 9 mg/mi which is slightly higher than the fresh catalyst. The car was not tested in a malfunction mode with the aged catalyst.

The test results for this car are given in Table 12 for the FTP.

GM did not specify the rhodium content of the 3-way catalysts tested. However, HCN emissions from these catalysts are much lower than those found for the Volvo 3-way catalyst systems.

C. Ford Work

Ford has done more extensive work on HCN emissions than any other automobile company to date.

The initial Ford work involved lengthy validation of both the pyridine-pyrazolone and the ion selective electrode method for HCN. Both of these methods can be used to analyze HCN trapped in a potassium hydroxide solution contained in a bubbler. Ford bubbles a small sample from their dilution tunnel into the bubbler. The first test done by Ford showed the injection of 6.74 ppm HCN, approximately 90 mg/mi, resulted in 93.8% HCN recovery. The tests were repeated with lower levels of HCN injected. Quantities of HCN corresponding to 3.14 ppm or approximately 45 mg/mi resulted in poor recovery, the reasons for which are unknown at the present time. Ford then added known quantities of HCN to the dilution tunnel stream when a vehicle was being tested at a 45 mph cruise condition. These tests showed an HCN recovery rate of only 50% indicating an interference problem with both methods. Ford work identified the problem to probably be a low concentration of potassium hydroxide in the bubblers (caused by reaction of acidic exhaust components) which allowed HCN to escape. Modifying the method by using more hydroxide resulted in a recovery of 94% of the HCN. Ford work shows the limit of detection of both methods is about 0.06 mg/mi of HCN. While more work is needed to refine the method, the method as it stands now can be used for reasonable approximation of automotive HCN emissions.

Ford vehicle tests were conducted on a Granada equipped with a 302 CID engine and a 3-way catalyst followed by an oxidation catalyst (Vehicle 9P), a Pinto equipped with a 2.3 litre engine with a similar system, and a 1978 prototype Pinto with a 3-way catalyst.

TABLE 12

HCN Test Results of 3-Way Catalyst Vega

<u>Test Condition</u>	<u>HC gm/mi</u>	<u>CO gm/mi</u>	<u>NOx gm/mi</u>	<u>HCN mg/mi</u>	<u>NH₃ mg/mi</u>
Fresh Catalyst -- closed loop	0.29	2.8	0.23	2	2
open loop -					
6% rich	0.30	3.4	0.86	2	3
12% rich	0.83	19.7	0.13	16	211
18% rich	1.75	60.0	0.11	11	259
50,000-Mile Catalyst -- closed loop	0.63	5.36	0.60	9	8

Tests on the Granada were conducted with the air injection functioning normally and with the air injection after the 3-way catalyst disconnected simulating a rich malfunction condition. This car was tested over the CFDS, idle, and 45 mph steady state conditions. With the air pump disconnected, HCN emissions were 12.3 mg/mi compared to about 0.15 mg/mi with the air pump functioning. CO emissions over the CFDS were about 16 gm/mi with the air pump disconnected and only 2 gm/mi with the air pump functioning.

The Pinto (Vehicle T791) with the 3-way plus oxidation catalyst system was tested under the same conditions as Vehicle 9P. The HCN emissions were under 5 mg/mi for all tests. CO emissions were extremely low both with the air pump disconnected (under 0.1 gm/mi) and with it functioning correctly (also under 0.1 gm/mi). It is possible that the low CO on Vehicles 9P and T791 are partly responsible for the low HCN formation.

The 1978 3-way catalyst prototype (Vehicle 61E28) was tested with a line to the carburetor being plugged to deactivate the oxygen sensor. This resulted in a 12:1 air-fuel ratio. The vehicle was also tested in a 13:1 air-fuel ratio configuration. The car was tested under under idle (slow and fast), 50 mph, the CFDS, a hot start FTP, and the FET. HCN emissions were in all cases under 2 mg/mi. However, CO emissions were considerably higher than usual (96, 113, and 88 gm/mi over the CFDS, hot start FTP, and FET) giving ample opportunity for HCN formation.

Finally, Ford has done some laboratory studies with catalyst samples in their pulse flame reactor and also with simulated exhaust gas samples blended from gas cylinders.

The simulated exhaust gas experiments showed that higher NO and CO concentrations caused higher HCN formation as expected. Maximum HCN from a Pt-Pd PTX catalyst and a pure platinum catalyst is formed at 550°C. The temperature for maximum HCN formation is slightly lower for a rhodium-containing catalyst. Space velocity (from 20,000 to 200,000 hr⁻¹) did not influence HCN formation at 550°C. It should be noted that the simulated exhaust contained NO, CO, and hydrogen but no water vapor (a component normally found in vehicle exhaust).

However, the pulse flame reactor tests show that roughly the same amount of HCN is formed from 550° to 800°C for all of the catalysts tested (except one containing iridium). Additional tests showed that lower space velocities decrease HCN formation. The pulse flame apparatus results may be different from the laboratory test apparatus results because the gas used in the former experiments contained water vapor.

D. Chrysler Work

The initial Chrysler work on HCN consisted of running engine dynamometer tests with a variety of catalysts. Catalysts tested included an Engelhard Pt/Rh and three Chrysler catalysts (Pt, ruthenium-perovskite, and Pt/Rh). These tests were run with 1.5% to 5% CO (mostly 5%). Even though the CO levels were high, less than 1 ppm of HCN was formed. Chrysler even ran an engine dynamometer test with the catalyst at 1300°F where they thought HCN formation would be a maximum. Again, almost no HCN was formed.

Chrysler then decided to run some basic laboratory tests with simulated exhaust gases. Using a gas containing 3% CO, 1% hydrogen, and 0.2% NO in nitrogen, the following results were obtained with different catalysts.

Further tests with the platinum-rhodium catalyst shows that doubling the CO input also doubles the HCN emissions. Doubling the NO input also increases the HCN emissions but by less than a factor of two.

Chrysler did some further tube furnace laboratory studies involving the platinum-rhodium catalyst in one furnace and a platinum catalysts in a second furnace (in series). Such an arrangement approximates a dual catalyst system (a reduction catalyst followed by an oxidation catalyst). On a dual catalyst system, an air pump provides air injection after the reduction catalyst but before the oxidation catalyst. A vehicle air pump failure can be easily simulated in the tube furnace by not adding air between the two furnaces. Chrysler did this and varied the temperature of the oxidizing catalyst. The results shown in Table 14 were obtained using two different feedgases. These results show the greatest HCN emissions at about 1300°F.

Finally, Chrysler reports some work done on analytical methods. Chrysler uses the Liebig titration, the pyridine-pyrazolone method, and the selective ion electrode method. Chrysler states that heavy metals (nickel, copper, iron, and zinc) and the sulfide anion interfere with the selective ion electrode. However, Chrysler finds no evidence of any of these interfering species in the liquid impinger sample they collected.

E. Conclusions

Early studies by EPA showed HCN emissions from vehicles with 3-way catalysts operated under malfunction conditions. These emissions were always under 150 mg/mi for any driving mode and under 5 ppm for idle. Almost no HCN emissions were found from vehicles with 3-way catalysts under normal operating conditions. EPA has concluded that these levels of HCN do not represent a health concern.

TABLE 13

Chrysler HCN Laboratory Studies

<u>Catalyst</u>	<u>HCN (ppm)</u>
platinum-rhodium	72
platinum	0.9
ruthenium-perovskite	0.5
rhodium	160

TABLE 14

Chrysler HCN Laboratory Studies

<u>Feedgas A¹</u>		<u>Feedgas B²</u>	
<u>Temperature</u>	<u>HCN (ppm)</u>	<u>Temperature</u>	<u>HCN (ppm)</u>
600°F	67	750°F	1
800°F	65	900°F	3
1000°F	67	1050°F	9
1300°F	114	1200°F	49
		1350°F	92
(oxidizing catalyst removed)	65	1500°F	88

¹Feedgas A: 1.9% CO, 0.8% hydrogen, 0.19% NO, rest nitrogen

²Feedgas B: 0.7% ammonia, 1.9% CO, 0.8% hydrogen, rest nitrogen

The manufacturers have done extensive work developing analytical methods to measure HCN emissions. Also, considerable work was done measuring HCN on a number of non-catalyst and catalyst cars. Non-catalyst cars have been found to emit from 11-14 mg/mi of HCN. Oxidation catalyst cars emit far less HCN than non-catalyst cars even under malfunction conditions.

Therefore, currently available data indicate HCN emissions from catalyst cars is not a problem. However, HCN measurements should, of course, be done on future emission control systems as they are developed.

IV. RUTHENIUM EMISSIONS

A. Introduction

Ruthenium is being considered by several companies for use in catalysts. Chrysler has considered it for reduction catalysts, 3-way catalysts, and start catalysts. Ford has conducted extensive work with ruthenium for use in reduction catalysts. In addition, both Exxon and Gulf had done work in the past on ruthenium-containing reduction catalysts but are not now conducting any further work. The basic reason ruthenium is being considered is its low cost and attractiveness for nitrogen oxide control. Ford has considered use of ruthenium in the past for NO_x reduction catalysts and is currently considering ruthenium as a possible component of 3-way catalysts.

The higher oxides of ruthenium (RuO₄) are volatile and easily formed under oxidizing conditions. Various companies in previous years (Ford and Exxon) have tried to stabilize ruthenium so that it is not lost from NO_x reduction catalysts. These attempts were unsuccessful due to high loss of catalytic activity in the process or the loss of ruthenium. Recently, DuPont has worked on stabilizing ruthenium in a rare earth oxide perovskite structure. This work is still in progress. Since ruthenium oxides are very toxic, it seems that use of ruthenium catalysts depends on no significant emission of their oxides. EPA is not currently in a position to quantify what, if any, levels of ruthenium emissions would be considered significant. EPA health effects studies are investigating the toxicity of ruthenium and ruthenium oxides.

B. Chrysler

Chrysler is the only company to have reported studies on ruthenium emissions. Chrysler ran dynamometer and vehicle tests. Chrysler also sent the vehicle they tested to Exxon for independent tests. The dynamometer tests showed from 14 to 36 mg/km of ruthenium being emitted. At this rate, all of the ruthenium would be lost in 32,000 miles.

Chrysler has also conducted ruthenium tests on Research Car 232. Car 232 contains a small (58 cu. in.) ruthenium perovskite monolith catalyst close to the exhaust manifold. This catalyst can function as a reduction catalyst. A conventional Pt oxidation catalyst follows the reduction catalyst. Particulate samples were collected from the dilution tunnel using a Fluoropore filter which was analyzed for ruthenium by neutron activation. This car was run on AMA durability for 25,000 miles. The Chrysler tests indicated significant ruthenium loss. After 25,000 miles, the car was sent to Exxon for particulate tests. These tests showed again that ruthenium was being emitted at a substantial rate (about 150 mg/mi). The Exxon results were about three times higher than the Chrysler results. The Chrysler results indicated that all of the ruthenium on the catalyst would be lost in about 30,000 miles (if the emission rate were constant).

C. Conclusions

Tests by Chrysler show that ruthenium is in fact lost from ruthenium-containing catalysts. While ruthenium is not being used in any production catalysts currently, it is being considered for future catalysts so that the health impact of these emissions can be determined.

V. AMMONIA

A. Introduction and EPA Work

Ammonia emissions have been known to occur for some time now with dual catalyst systems under rich operating conditions. With a dual catalyst system, ammonia formed over the reduction catalyst is frequently reoxidized to NO over the oxidation catalyst. Ammonia formation in a dual catalyst system thus generally results in loss of NO control. It is possible to have incomplete oxidation of the ammonia over the oxidation catalyst which could result in significant ammonia emissions. Also, an oxidation catalyst system malfunction (e.g., air pump failure) can result in significant ammonia emissions.

In addition to possible ammonia formation with dual catalysts, ammonia can be formed with 3-way catalyst systems. Early EPA data show that the Volvo 3-way catalyst can have significant ammonia emissions under rich malfunction conditions. Data obtained by EPA-ORD and Exxon on ammonia emissions was given in detail in some of the tables in the HCN section. Essentially, these data showed 20-30 mg/mi ammonia under cyclic operation conditions with the vehicle correctly tuned and as high as 300-500 mg/mi under rich operating conditions.

Ford points out in their status report that ammonia will be emitted from their 3-way catalyst systems. Ford has also asked EPA from time to time on what level of ammonia emissions would be acceptable from a health standpoint. EPA is currently investigating possible health effects from automotive ammonia emissions including both entire air quality regions and localized situations (e.g., indoor parking garages and heavily traveled freeways). Currently, there is inadequate information to permit determination of the level of automotive ammonia emissions that would be acceptable.

B. Ford Work

Ford routinely measures ammonia emissions in all of their 3-way catalyst screening work. A parametric study performed by Ford on catalysts identical in all aspects but Pt/Rh ratio shows a linear decrease of net NO_x conversion (which is inversely related to ammonia formation) with increasing Pt/Rh ratio.

Laboratory studies of various catalysts show increasing ammonia formation as the A/F ratio becomes "richer" in the laboratory pulsator apparatus. For example, catalyst M268A shows an increase in ammonia formation from 0% of total NO_x to 20% as the A/F ratio changes from 14.38 to 14.08. Catalyst M268B shows a change in ammonia formation of only 0% to 2% under these conditions. Catalyst M275D2 produces from about 0% to 40% ammonia as the A/F ratio is changed from 14.48 to 14.08. These tests were generally run at 550°C.

Ford has also done some ammonia measurements of 3-way catalysts being durability tested. Testing was done with isooctane containing 0.007 gm/gal lead, 0.0008 gm/gal phosphorus, and 0.02% sulfur. As the catalyst ages, the A/F ratio units for optimum NO , CO , and HC conversion generally shifts about 0.1 A/F units to the rich side. Ammonia formation was noted to decrease significantly in some of the catalysts (M-270 and M-273), thereby aiding net NO_x conversion.

Ford also reported some engine dynamometer work on ammonia formation with catalysts containing differing amounts of rhodium. The results were those obtained in the laboratory apparatus mentioned earlier. These tests showed the ammonia formation was found to be inversely proportional to the rhodium content of the catalyst. Perhaps sulfur poisoning of the aged catalyst results in different ammonia formation characteristics than a fresh catalyst.

Finally, Ford reported ammonia formation characteristics of an experimental 3-way catalyst containing 3% TiO_2 (titanium oxide). The TiO_2 apparently affects oxygen storage capacity and the rates of oxygen transfer. The ammonia formation from this catalyst was very high, 26% at a point 2% rich of stoichiometric.

C. GM Work

Last year GM reported that ammonia emissions from four catalyst prototype vehicles are 1-3 mg/mi over the FTP, as shown in Table 15.

GM work on 1975 production cars without air injection under rich malfunction conditions show ammonia emissions of 43-165 mg/mi. In this year's status report, GM reports ammonia emissions on a 1975 Vega with a 3-way catalyst. Since this car was also tested for HCN emissions, the ammonia test results were given previously in the HCN section. This car showed 2-8 mg/mi of ammonia under normal operating conditions, 3 mg/mi when operating 6% rich, and 211-259 mg/mi when operating 12-18% rich.

GM also tested four 1975 catalyst cars and one 1974 non-catalyst car for organic amines over the FTP. Amine compounds are very similar to ammonia. No amine emissions were found using the wet chemistry iodometric analysis method which has a limit of detection of 2 mg/mi.

D. Conclusions

Ammonia emissions may be significant from vehicles with 3-way catalysts but only under malfunction conditions. Ammonia emissions should be measured from vehicles with 3-way catalysts as they are being developed.

Ammonia emissions from vehicles equipped with oxidation catalysts do not appear to be significant.

VI. POLYNUCLEAR AROMATIC COMPOUNDS (PNA)

A. Introduction

Polynuclear aromatic compounds (PNAs) are of interest due to their carcinogenicity. The PNAs are a group of multi-ring aromatic hydrocarbon compounds with very low volatility and high molecular weight. About 90% of total PNAs in the atmosphere come from stationary sources (in particular from coal burning). Only about 10% of the total PNAs come from mobile sources. Even though little PNA work has been done on diesels, it is estimated that about half of this 10% comes from diesels. The other half of the 10% comes from other motor vehicles.

TABLE 15

GM Ammonia Data

<u>Car</u>	<u>Catalyst</u>	<u>Ammonia (mg/ml)</u>
O-39680	HN 2236	3
O-38608	HN 2236, AIR	2
E564346	HN 2221 and 2364 (dual catalyst, reduction and oxidation)	1
C4361	HN 2217 and 3059 (3-way and oxidation catalyst, closed loop fuel injection)	2

Sometimes benzo(a)pyrene (BaP) is measured by itself instead of measuring total PNAs (which consist of about 20 compounds). The amount of BaP found can generally be correlated to total PNAs. BaP is relatively easy to measure and is more carcinogenic than most other PNAs.

PNA compounds in automotive exhaust have been studied for some time. Early contract work through CRC-APRAC from 1968-72 thoroughly characterized PNAs. This work was done at Exxon and involved testing several cars. It was found that post-1968 cars had about half the PNA emissions of pre-1968 cars. The control of HC and CO also resulted in decreases of PNA. Exxon did some work on prototypes equipped with advanced catalysts and thermal reactors. Both systems were found to greatly reduce PNAs (generally by 95% or more compared to uncontrolled vehicles. Subsequent work by UOP showed that catalysts preferentially oxidize PNA compounds resulting in very low PNA emissions from vehicles with catalysts.

Very little work has been done on measuring PNAs from light-duty diesels. However, work at Southwest shows heavy-duty diesels emit much greater quantities of PNAs than do gasoline engines. It is important that PNA work be done on light-duty diesels.

B. VW Work

The only PNA data reported in the submissions came from VW.

Volkswagen (VW) presented an interesting summary and discussion of their testing concerning the levels of PNA from different types of emission control technologies, alternative engines, and alternative fuels. VW did not provide complete details concerning the test procedures utilized in VW's testing for PNAs. Also missing from the VW discussion was any mention of PNA emissions from diesel engines.

VW reported that their studies showed extremely low levels of PNA concentrations in automobile exhaust emissions. These levels are reported to be approximately 0.001 gm/km (0.0016 gm/mi) on the European Emission Test Procedure. This level is higher than found by other investigations.

In addition to utilizing the European Test Procedure, the data were collected under the following conditions:

- (1) Europe Fuel ERF-G1 was used in all procedures. This type of fuel has a composition of 55% paraffins, 8% olefins, and 37% aromatics. Its lead content is 0.71 gm/litre (2.68 gm/gal). Lead-free fuel (VK 91) was used with noble metal catalyst-equipped engines. The lead-free fuel contains 1% more aromatics.

- (2) The motor oil was a standard brand heavy duty oil. The oil was changed before every PNA test to avoid PNA enrichment of engine oil.
- (3) The test vehicles had accumulated between 2,000 and 15,000 miles of city driving at the start of the test.

Volkswagen presented the data in Figure 1 which illustrates the distribution by percent of PNAs in automobile exhaust emissions produced by a variety of engine design concepts. The column labeled "Carcinogenic properties" is VW's estimate of the relative severity or danger of producing cancerous effects in humans. This opinion does not reflect EPA's position indicating which PNAs are more carcinogenic than others. It should also be noted that the PNA listed in Figure 1 are less stable as they proceeded down the list and hence easier to break down with exhaust aftertreatment.

Volkswagen drew the following conclusions concerning PNA from vehicles equipped with gasoline-fueled engines.

- (1) There is a certain and insignificantly varying pattern of distribution of the measured ten individual PNA components from fluoranthene through coronene. The lower four-ring PNAs represent approximately 80% of this pattern. VW mentioned that among the ten measured PNA components there are three each which combine two or three individual PNA components. There is one triplet each in the chrysene and in the benzo[fluoranthenes], and one twin in the idenopyrene.
- (2) The present production vehicles produce the following scatter on European Test Procedure - PNA total emissions of between 2000 $\mu\text{gm}/\text{test}$ and 10,000 $\mu\text{gm}/\text{test}$, and between 50 $\mu\text{gm}/\text{test}$ and 215 $\mu\text{gm}/\text{test}$ in the benzo(a)pyrene emissions.
- (3) The following percent reduction of PNA emissions are obtained with other concepts when compared to gasoline-powered vehicles.

production vehicles	=	100%
catalytic design concepts	=	5%
thermal reactor concepts	=	15%
methanol vehicles	=	10%

PNA	CARCINO- GENIC PROPERTIES + SLIGHT ++ MEDIUM +++ STRONG	VEHICLE CONCEPTS			
		PRODUC- TION VEHICLES	CATALYTIC CONCEPTS	THERMAL REACTOR CONCEPTS	METHANOL VEHICLES
		% OF TOTAL PNA			
FLUORANTHENE	0	24	22	25	37
PYRENE	0	38	28	32	42
CHRYSENE + M 226 + BENZO(A)ANTHRACENE	+	20	15	13	8
BENZOFLUORANTHENE	++	3	5	5	3
BENZO(E)PYRENE	+	2.5	4	4	2
BENZO(A)PYRENE	+++	2.5	2.5	2.5	1.5
PERYLENE	0	0.5	0.5	0.5	0.3
INDENOPYRENE + DIBENZ(AH)ANTHRACENE	+	2	4	2	1.5
BENZO(G,H,I)PERYLENE	0	7	11	9	3
CORONENE	0	4.5	9	7	2

% DISTRIBUTION OF TOTAL PNA	100%	5%	15%	10%
TOTALS IN VARIOUS PRODUCTION VEHICLES IN $\mu\text{g}/\text{TEST}$	2,000 to 10,000			

PERCENT SHARE OF CARCINO- GENIC PNA'S	APPROXIMATELY 20 TO 30%
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Figure 1. PNA percent distribution in exhaust emissions, European test.

- (4) The distribution pattern of vehicle concepts other than production vehicles show limited but characteristically shifted PNA patterns. The four-ring PNAs are lower in catalytic concepts than in the thermal reactor concepts while the six and seven-ring benzo(ghi)perylene and coronene components show a distinct increase in the catalytic concepts. This indicates that these afterburner concepts reduce the latter components less when compared with the lower PNAs.

On the other hand, engines operated on methanol show an extremely strong presence of 80% of the lower four-ring fluoranthene and pyrene components. This means that the absence of the PNAs and of the other aromatic components in methanol fuel not only produces a PNA emission that has been reduced by one order of magnitude but that higher PNA synthesizing is impeded.

- (5) The investigation shows the total of the more or less carcinogenic individual components (as far as such carcinogenic effects are known from various (sources) to amount to approximately 20% or 30% per volume of total PNA emission.

VW produced another graph (Figure 2) which shows the results obtained with an engine using propane and gasoline. VW notes that propane operation reduces the PNA content to 10% (similar to methanol operation) when compared with gasoline operation.

VW feels this fact permits an interesting conclusion in regard to the influence of engine oil, i.e., that engine oil influence on PNA emissions in gasoline operation is bound to be lower than 10%. VW stated that it is of additional interest that identical hydrocarbon emissions were measured in the European Test Procedure under both modes of operation. They feel this confirms the experience found elsewhere in a great many areas that the level of hydrocarbon emissions can not be used to draw conclusions about PNA emissions.

Another interesting graph (Figure 3) from VW presents the PNA emissions compared to CO emissions. This graph shows the results obtained from different gasoline engine-equipped vehicles. Each point represents one test vehicle. The graph allows for the following VW findings:

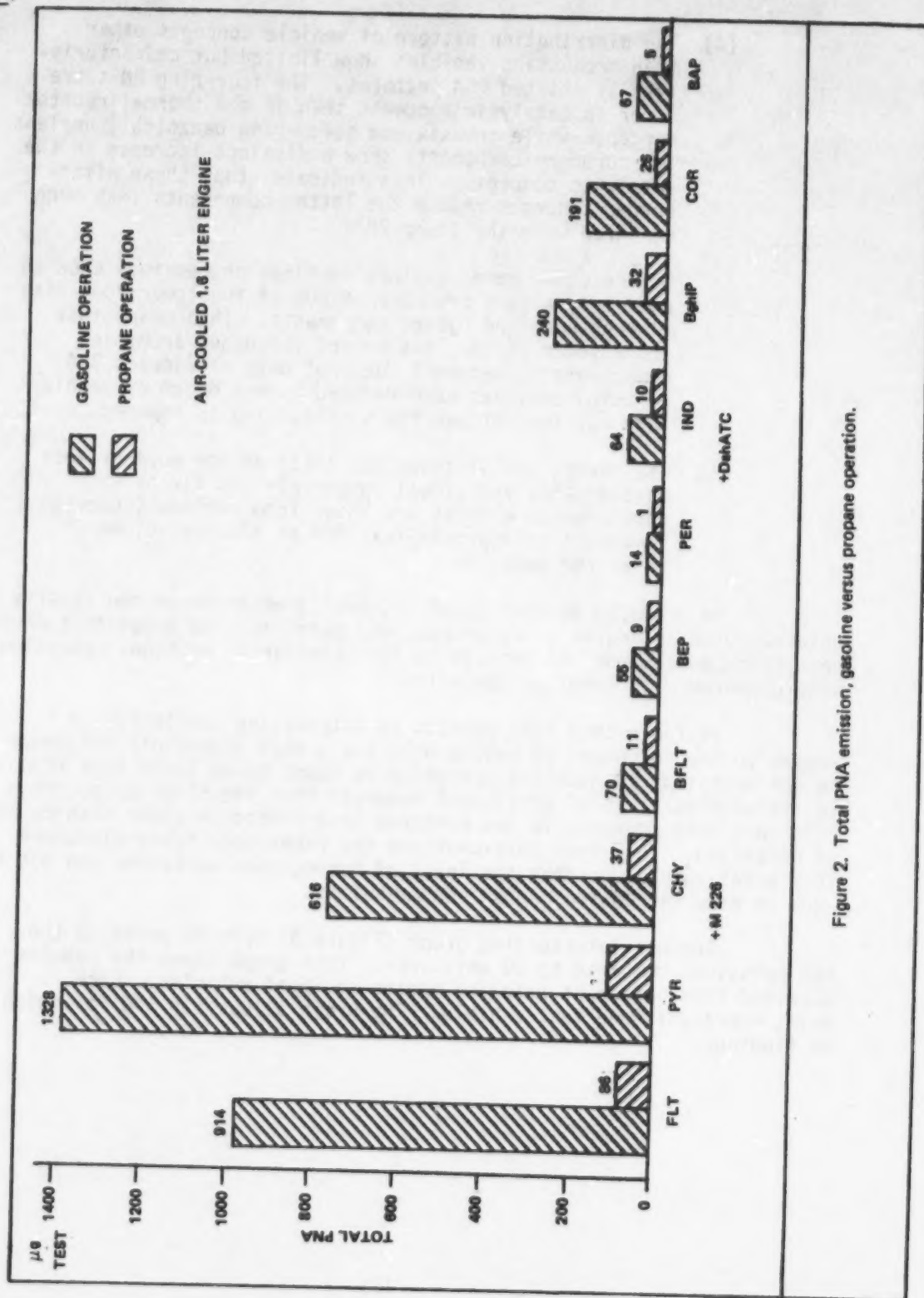


Figure 2. Total PNA emission, gasoline versus propane operation.

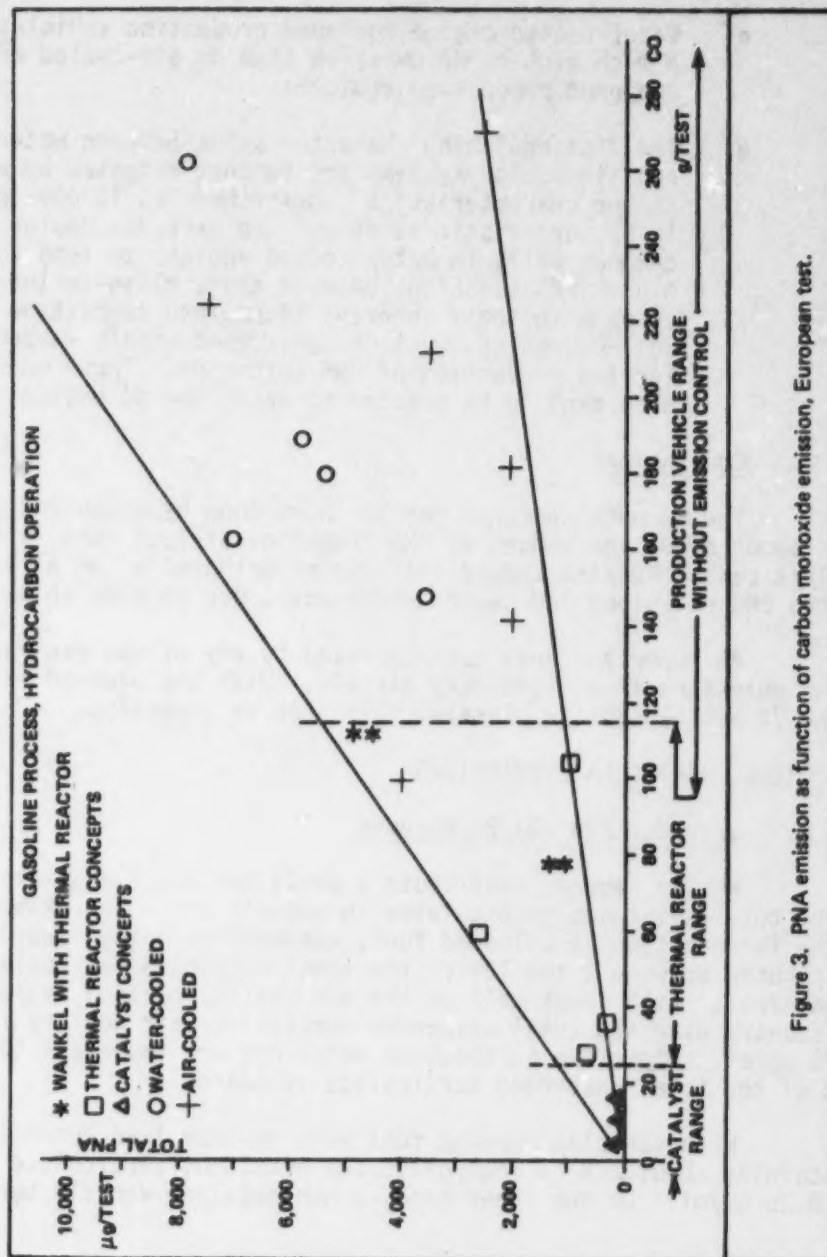


Figure 3. PNA emission as function of carbon monoxide emission, European test.

- All measuring points are located in a band that spreads with the increase in CO emissions, and the upper limit of which is set by the ascending slope of approximately 5000 $\mu\text{gm PNA}/100 \text{ gm CO}$ and the bottom limit by 1000 $\mu\text{gm PNA}/100 \text{ gm CO}$.
- Water-cooled engine-equipped production vehicles produce a much higher PNA emission than do air-cooled engine-equipped production vehicles.
- The distinguishing characteristics between water-cooled and air-cooled systems are further affected by additional engine characteristics. Nevertheless, it does not appear to be unrealistic to expect the markedly cooler combustion chamber walls in water-cooled engines to tend to produce higher PNA emissions because these close-to-the-wall zones with their inherent incomplete combustion due to wall-quenching, must be considered highly responsible for the production of PNA emissions. These quench zones also tend to be greater in water-cooled engines.

C. Conclusions

The VW work confirms earlier work done by Exxon and UOP which shows about 5% of the amount of PNA from non-catalyst cars is found in catalyst cars. VW also showed that use of methanol as an alternate fuel reduces PNA emissions and causes different types of PNAs to be emitted.

An important area not addressed by any of the manufacturers is PNA emissions from light-duty diesels. With the planned introduction of the VW and Oldsmobile diesels, this area is important.

VII. DIESEL PARTICULATE EMISSIONS

A. Introduction and Background

Mobile sources contribute a small but still significant part of the total suspended particulates in ambient air. For example, prior to the introduction of unleaded fuel, automobiles using leaded fuels contributed between 2 and 13% of the total suspended particulates in urban areas. With about half of the air quality control regions around the country over the total suspended particulate air quality standard of 75 $\mu\text{g}/\text{m}^3$, automotive particulate emissions are important to the attainment of the total suspended particulate standard.

With vehicles burning fuel with maximum lead concentrations (containing about 2.5 gm lead/gal), the resultant particulate emissions are 0.25 gm/mi. On the other hand, a non-catalyst vehicle burning

unleaded fuel emits only 0.01 gm/mi of particulate. Catalyst-equipped vehicles emit much less particulate vehicles burning unleaded fuel. An approximate particulate emission rate for these catalyst cars is 0.02 gm/mi and is based on testing of over 100 cars. Particulates from non-catalyst vehicles burning unleaded fuel consist mostly of high molecular weight organic compounds. Particulates from catalyst cars burning unleaded fuel consist primarily of sulfuric acid and its water of hydration.

As the use of unleaded fuels in catalyst-equipped vehicles displaces the use of leaded fuels (which emit 0.25 gm/mi particulates), the automotive contribution to urban air total suspended particulates will decrease from 2-13% to about 0.2-1.3%.

The introduction of large numbers of light-duty diesels may reverse this trend and increase the automotive contribution to total suspended particulates. Therefore, it is important to investigate the quantity of diesel particulates emitted.

B. Composition of Diesel Particulates

The composition of light-duty diesel particulates has not been completely determined. It is known that a major constituent of these particulates is elemental carbon with the ability to adsorb other compounds on it much like activated charcoal. The types of compounds that have been found adsorbed are SO_2 , sulfate, high molecular weight organic compounds, and polynuclear aromatic hydrocarbons.

The quantity of hydrocarbons including polynuclear aromatics (PNA) present in diesel particulates is currently being investigated by EPA in contracts with Southwest Research Institute (SwRI). A problem impeding progress in this area is that the sampling and collection procedures are in a rudimentary stage of development, particularly for PNA. Some measurements are currently being conducted for one PNA species, benzo(a)pyrene, in light-duty diesels under the EPA contract work with SwRI. Also, PNA emissions were investigated to some extent by a previous CRC contract with Gulf Research.

The amount of sulfate in diesel particulate has been determined accurately by EPA work (both in-house and contract work) and found to represent only a small fraction (about 1-2%) of the sulfur in diesel fuel. While this conversion to sulfate is about the same for the diesel as for non-catalyst gasoline cars, diesel sulfate emissions are greater than those from non-catalyst gasoline cars (0.1 vs. 0.01 gm/mi) due to the higher sulfur content of diesel fuel compared to gasoline (about 0.23% vs. 0.03%). Still, sulfate emissions account for a very small part of the total particulates from diesels.

There is some overlap between diesel particulate and hydrocarbon measurements. Some of the compounds measured as gaseous hydrocarbons by the heated FID (at 375°) used in the Federal Test Procedure are also collected as particulates since the dilution tunnel filter is about 120°F. The amount of overlap has not been quantified accurately, but some fraction of the particulate is being measured and subject to the HC emissions standards.

Diesel particulates are very small in size with most of the diesel particulates below 1 micron in size. Attempts to determine the size distribution by impactors have not been successful since impactors separate particulates from 1 to 10 microns in size. This information on particulate sizes is important to the determination of how far they penetrate into the respiratory system.

The health effects associated with diesel particulates have not been determined. EPA has a contract with SwRI to do some bioassay tests on diesel particulates and is also doing some in-house animal tests in Cincinnati.

C. Quantity of Diesel Particulates

Almost all of the work done to obtain emission factors on light-duty diesels has been done by EPA either through contract or in-house testing. Little data have been provided by the manufacturers.

These programs have employed the standard dilution tunnel approach to measurement. Tests completed to date have included the vehicles shown in Table 16. The results are shown in the table.

The Oldsmobile prototype tested by EPA is similar to but not identical to the version being considered by GM for production in 1978. EPA contract work at SwRI involved testing a number of diesel vehicles.

Particulate emissions rates are given for several cycles including the FTP, CFDS, and FET. Of special interest are the FTP results, since this driving schedule represents driving patterns in an air quality control region as a whole. Since gaseous emissions over the FTP are used in air quality models and for emission factors in the EPA booklet, AP-42, particulate emissions factors over the FTP can be used likewise. The CFDS represents congested freeway driving while the FET represents rural-highway-type driving.

Table 16

Particulate Emission Rates of Light-Duty Diesel Vehicles

Vehicle/Model	Engine Disp. (CID)	Inertia wt (lbs)	Test Lab	FTP Gaseous Emissions				Sulfates mg/mile SET	Particulates g/mile		Fuel Eco. (MPG)	
				HC g/mile	CO g/mile	NOx g/mile			FTP	SET	FEI	FTP
1. Mercedes 220D	134	3500	SwRI	0.18	1.30	1.05		9.21 ¹	0.60	0.43	31.5	25.9
2. Mercedes 240D	146	3500	SwRI	0.29	0.97	1.27		14.12 ¹	0.48	0.36	33.7	25.7
3. Mercedes 300D	183	4000	SwRI	0.16	0.85	1.72		16.53 ¹	0.49	0.37	30.0	23.8
4. Peugeot 204D	83	2500	SwRI	1.11	1.71	0.68		8.21 ¹	0.38	0.24	43.8	35.9
5. Perkins 6-247	247	4500	SwRI	0.72	2.87	1.50		18.26 ¹	0.81	0.49	28.3	25.7
6. VW Diesel*	90	2250	SwRI	0.37	0.79	0.87		7.02	0.29	0.26	53.7	42.7
6a. VW Gasoline			SwRI	0.23	3.70	1.01		1.65	0.007	0.002	36.1	24.6
7. Oldsmobile Diesel	350	4500	SwRI	0.76	2.00	1.13		16.62	0.92	0.58	2	2
7a. Oldsmobile Gasoline*	260	4500	SwRI	0.39	2.16	1.37		20.90	0.009	0.016	23.0	15.5
8. Pinto Diesel		2750	AA	0.24	1.21	0.76		8.53	0.35	0.38	54.5	44.8
9. Postal Van Diesel	165	3000	AA	0.14	1.47	2.54		10.14	0.47	0.27	37.8	29.9
10. VW Rabbit Diesel	90	2250	AA	0.11	0.98	1.22		9.34	0.32	0.23	51.0	31.6
11. Chrysler Diesel	200	4500	AA	0.26	1.22	1.82		12.24	0.19	0.17	25.7	22.4
12. VW Rabbit Diesel	90	2250	AA	0.23	1.11	0.93		5.47	0.31	0.20	51.7	40.6
13. Mercedes 300D	183		AA	0.16	0.92	2.17		7.85	0.43	0.27	29.5	23.8
14. Oldsmobile Diesel	350	4500	AA	0.52	1.92	1.47		8.52	0.42	0.39	2	2
15. Nissan Diesel	122	3500	RTP	0.25	1.10	1.37			0.3		33.8	26.2
16. Peugeot 504	129	3000	RTP	0.49	1.45	2.30		7.0	0.51	.31	35.9	26.4

*Gasoline car included for comparison to diesel counterpart

¹ Sulfate values for these tests are over the FTP.² GM requested the diesel fuel economy for the Oldsmobile be kept confidential at this time.

The Mercedes 300D was tested by both SwRI and EPA. The particulate results obtained by EPA (0.43, 0.27, 0.25 gm/mi over the FTP, CFDS, and FET) agree well with those obtained by SwRI (0.49, 0.37, and 0.39 gm/mi over the FTP, CFDS, and FET). The gaseous emission numbers also agree well. The same Oldsmobile diesel was also tested at both labs but EPA did not obtain particulate mass measurements during the tests. The particulate numbers on the VW diesel from SwRI (0.29, 0.26, and 0.25 gm/mi over the FTP, CFDS, and FET) agree well with those obtained by EPA (0.32, 0.23, and 0.26 gm/mi over the FTP, CFDS, and FET). The gaseous emission results between the two laboratories on the VW agree reasonably well, but the HC at EPA (0.11 gm/mi) is lower than that found at SwRI (0.37 gm/mi).

The four tests on the three Mercedes vehicles tested gave an average particulate mass of 0.50 gm/mi over the FTP. The two Peugeot vehicles tested gave 0.45 gm/mi of particulate over the FTP. The Nissan had particulate emissions of 0.30 gm/mi. The VW Rabbit diesel also had particulate emissions of 0.30 gm/mi. This level of particulate emissions is still over 40 times the level found from the VW gasoline prototype. The Oldsmobile diesel emitted a relatively high level of particulates (0.92 gm/mi over the FTP). This level is 100 times the level found from the gasoline counterpart (an Oldsmobile 350 gasoline vehicle). However, GM states that this Oldsmobile diesel is a prototype and may be changed before final production.

The two gasoline counterparts (Oldsmobile and VW) had somewhat lower particulate emissions than found for vehicles equipped with catalysts (generally 0.02 gm/mi). The 0.02 gm/mi number is based on extensive tests of over a hundred cars and should be considered a number for general comparison of gasoline and diesel cars. For individual models, it is more appropriate to use numbers from diesel-gasoline counterparts if available.

The average particulate emissions from the four tests on the three Mercedes, the two tests on the VW, the test on the Oldsmobile, the two Peugeots, and the Nissan are about 0.5 gm/mi over the FTP. The number can be used as an approximate diesel particulate emission factor for air quality models. It can be updated as more data are available. The numbers from the experimental vehicles (Pinto, Postal Van, and Chrysler diesels) were not included in this average but would not significantly change it.

D. Conclusions

Tests conducted to date show very high particulate emissions from light-duty diesels (0.5 gm/mi) which is about 25 times comparable values for gasoline vehicles equipped with catalysts (about 0.02 gm/mi).

The particulates consist of elemental carbon as well as various hydrocarbon compounds and small quantities of sulfate. EPA does not know yet what the health effects of these particulates are.